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# NBS TECHNICAL NOTE 585

## Microchemical Analysis Section:

Summary of Activities  
July 1970 to June 1971

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UNITED STATES DEPARTMENT OF COMMERCE  
Maurice H. Stans, Secretary  
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, Director



# TECHNICAL NOTE 585

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## **Microchemical Analysis Section: Summary of Activities, July 1970 to June 1971**

John K. Taylor, Editor

Microchemical Analysis Section  
Analytical Chemistry Division  
Institute for Materials Research  
National Bureau of Standards  
Washington, D.C. 20234



NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.



## FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 57 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.



Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1971 we plan to issue these summaries for all of our sections. The following is the seventh annual report on progress of the Microchemical Analysis Section.

W. Wayne Meinke, Chief  
Analytical Chemistry Division

## PREFACE

This report summarizes the current program and recent activities of the Microchemical Analysis Section of the Analytical Chemistry Division. This Section has the primary mission to contribute to the science and technology of the analysis of small samples and its program includes both fundamental studies to improve the precision, accuracy and sensitivity of analytical techniques, and developmental research to provide new and improved methods applicable to wide areas of materials characterization. As a closely related activity, the Section provides analytical measurements for various research programs of the Bureau and develops and characterizes Standard Reference Materials. Research projects are active in the following areas: gas analysis; atmospheric pollution analysis; and conventional microchemical analysis.

A major effort of the Section during the year has been concerned with the analysis of Standard Reference Materials. No effort has been spared to characterize these materials to a high degree of reliability. The use of such materials not only establishes benchmarks for industrial control but also provides a sound basis for inter-laboratory comparisons and for the intercomparison of measurement techniques and methodology. Such materials are regularly used in this laboratory to verify the accuracy of analytical procedures. They are referred to by an identification such as SRM 160b, for example. A catalog containing full descriptions of these materials may be obtained from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234.

A number of analytical methods developed or modified for the analysis of Standard Reference Materials as well as materials submitted by several NBS research projects are described briefly. Space limitations have dictated only a brief description of methods in most cases. It is hoped that such descriptions will be understandable to an experienced analyst. How-

ever, specific details of all work reported here will be made available to anyone interested in such matters. Some of the work discussed is a continuation of activities described in previous reports. Copies of the latter are available upon request in most cases.

In order to describe procedures, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

John K. Taylor, Chief  
Microchemical Analysis Section



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# MICROCHEMICAL ANALYSIS SECTION: SUMMARY OF ACTIVITIES

July 1970 to June 1971

Edited by John K. Taylor

This report describes the scientific program of the Microchemical Analysis Section of the Analytical Chemistry Division of the National Bureau of Standards, Institute for Materials Research during July 1970 to June 1971. General activities are reported in the areas of air pollution measurement standards including both gases and particulates, in the field of microchemical analysis, in fire research and in electrochemical analysis performed under an international research grant program. A sulfur dioxide standard reference material for use in monitoring ambient atmosphere, and the initial work on a similar standard for stationery sources are described. Research activities on potential standard reference materials for ozone, nitrogen dioxide, and carbon monoxide are also described.

Key words: Air pollution analysis; sulfur dioxide; carbon monoxide; ozone; nitrogen dioxide; fire research; microchemical analysis; particulate analysis.

## 1. INTRODUCTION

The scope of activities of the Microchemical Analysis Section has been changing during the past several years. The competences within the Section have always included techniques with considerable analytical applicability. Accordingly, the certification analysis of Standard Reference Materials (SRM's) and the analysis of research materials for other NBS programs has been a major activity. As a result, the Section's program has shown a high degree of flexibility, responding to both national needs and to the needs of the NBS research activity. A research program to provide improved measurement capabilities has been a logical compliment to these analytical activities.



The growing concern in the United States about air pollution has focused sharply the need for reliable determination of trace constituents in the atmosphere. Not only must such measurements be made more extensively than ever before, but legal enforcement considerations demand a high degree of compatibility between measurements made by different laboratories. The reliability required can only be achieved by the development of a national system of standard reference materials to which all measurements can be traced.

In recognition of this need, the Air Programs Office of EPA has sponsored a program at NBS for several years to help support the research and development aspects, and the NBS Office of Standard Reference Materials has devoted considerable resources to production of SRM's as they are developed. The Microchemical Analysis Section has been the main participant in this program. Accordingly, these activities play a dominant role in this year's Progress Report.

The Section has also become involved in some other activities closely related to the program mentioned above. A survey to determine the composition of the atmosphere encountered by fire fighters in burning buildings has been completed. An extensive project to evaluate analytical methodology and calibration procedures for measurement of toxic materials in industrial atmospheres was initiated under the sponsorship of the newly created National Institute of Occupational Safety and Health. This program will not be further described in the Report but will be deferred until the following year, since its activities have consisted in preliminary planning up to the present time. Activities in the area of water pollution measurements have also been initiated and it is expected that these will be expanded.

The Section has continued to be active in classical microchemical analysis and these activities are reported. The excellent work carried on at the Technion, Haifa, Israel, by Professor Ariel and her students, under the PL480 Program is also reported.

In light of the changing emphasis of the Section's activities, and also to consolidate electroanalytical programs, the Section's long established projects in coulometry and polarography have been transferred to the Electrochemical Analysis Section of this Division. Readers who have been following the course of these activities will find them reported in the Progress Report of that Section.

(John K. Taylor)

## 2. AIR POLLUTION MEASUREMENT STANDARDS

This Section has initiated a program to establish a compatible series of analytical reference standards for air pollution measurements related to the National Ambient Air Standards. Reference standards for sulfur dioxide and hydrocarbon measurements have recently been issued. Work on similar reference materials for use in measurement of carbon monoxide, oxides of nitrogen, and photochemical oxidants is now in progress and will be discussed in succeeding chapters.

The system consists in maintaining a group of reference materials or generators of specific pollutants, whose compositions or operational characteristics are known to a high degree of accuracy. The members of each group will be systematically and periodically evaluated, using state-of-the-art measurement techniques so that their composition or performance can be reliably predicted at any time. The reference standards will be intercompared, as possible, to validate the compatibility of the system. Standard Reference Materials or devices capable of generating calibrants will be compared with these analytical reference standards and distributed by the NBS Office of Standard Reference Materials.

Initial emphasis is being placed on pollutants related to ambient air measurements because of the air quality standards that have been promulgated. The system will be expanded to include emission levels, as well. Plans are now being made to provide an entire series of standard reference materials suitable for the calibration of automotive emission measurements. Because emissions from all sources must be introduced into a diffusion model to interpret ambient air quantity measurements, all of the analyses must be compatible. This is not achievable at present because of variations in measurement and calibration

procedures. The SRM's processed by NBS should make compatible measurements possible.

The need for compatible standards for analytical calibrations has been recognized by both government and industry. The Air Programs Office of EPA has provided substantial support to NBS in establishing the program and sponsoring the research back-up it requires.

(John K. Taylor)

### 3. SULFUR DIOXIDE STANDARDS

#### A. Sulfur Dioxide Permeation Tubes

A research project to evaluate the potential of permeation tubes to provide reliable calibrations of sulfur dioxide determinations at ambient levels was carried out during fiscal year 1970. This program was sponsored by the Air Programs Office of EPA and much of the results were published in the Summary of Activities for 1969-70 [1]. In brief, this work demonstrated the feasibility of this approach and established the basis for the calibration procedures used.

A standard reference material consisting of a 10 cm sulfur dioxide permeation tube was announced on December 1, 1970 and is available from the Office of Standard Reference Material (SRM 1625). These tubes have a typical SO<sub>2</sub> permeation rate of 2 µg/min at 25 °C. Two additional standards in this series will be available shortly. These consist of 5 cm and 2 cm sulfur dioxide permeation tubes and are designated SRM 1626 and SRM 1627 respectively. The typical permeation rates of these tubes are 1.0 µg/min and 0.4 µg/min, respectively.

The permeation tubes in these series are individually calibrated at three or more temperatures in the range between 20 and 30 °C. The primary calibration technique is by gravimetric determination of the weight loss due to SO<sub>2</sub> emission. However, selected tubes are calibrated by coulometric measurement, as described by Scaringelli [2]. The measured rates are computer fitted by the method of least squares to an equation of the type  $\log R = mt + b$ . The resulting equation is used to calculate rates at 1-degree intervals between 20 and 30 °C.

The precision of measurement is estimated from the results obtained on calibration of each lot, consisting of between 25 and 50 tubes. The calibration uncertainty for the 10 and 5 cm tubes is approximately 0.5 percent at 25 °C and less than 1 percent at the higher and lower temperatures. The uncertainty



for the 2 cm tubes is about 1 percent at 25 °C and 2 percent at either end of the temperature range.

The systematic errors concerned with the calibration are considered negligible. Variations are minimized by controlling the bath temperature to better than  $\pm 0.01$  °C and the weighings are made with a microbalance at sufficiently long time intervals that the uncertainty in weight losses is probably less than 5 parts in 2000.

These tubes are used to produce known concentrations of sulfur dioxide in air streams which are then used for the calibration of instruments designed principally for measuring ambient atmosphere concentrations of sulfur dioxide.

Apparatus and techniques for this purpose are described in references [3] and [4] and should be consulted for operational details. Because of the large temperature coefficient of the permeation rate, approximately 9 percent per degree celsius, the temperature must be maintained constant and measured accurately to 0.1 °C to provide concentrations consistent with the calibration uncertainty.

It is recommended that the tube temperature be held constant during use and that desired concentration levels be achieved by adjustment of the flow rate. If it is necessary to vary the concentration by changing the tube temperature, a suitable time interval must be allowed for equilibrium of the permeation rate to be re-established. For changes of 1 or 2 degrees celsius, a period of 3 hours should suffice. For changes of 10 degrees or when removed from low temperature storage, a period of 24 hours is advisable.

These tubes are stable and relatively rugged sources of sulfur dioxide and when properly used, the calibration should remain valid for the entire time that any visible liquid sulfur dioxide remains in the tube. At room temperature, the useful lifetime is about nine months but this can be extended by storage of the tube at low temperature

between periods of use. However, they should be protected from moisture during storage. On removal from low temperature storage, the tubes should be equilibrated at the operating temperature for at least 24 hours, before use as analytical standards.

#### B. Sulfur Dioxide Standards for Source Analysis

Analytical methods for the determination of high concentrations of sulfur dioxide in emission sources require calibration mixtures which cannot be conveniently produced, using permeation tubes. Mixtures containing low concentrations of sulfur dioxide in air are not sufficiently stable in ordinary gas cylinders to allow the use of such materials as standards in the part per million concentration range. It was anticipated that higher concentrations, 0.2 mole percent for example, would be unstable to some extent but it was hoped that the instability would be analytically harmless, if not insignificant.

Mixtures at the 2000 ppm concentration level were prepared in large cylinders and transferred to a number of small cylinders. The ratio of sulfur dioxide to nitrogen was determined mass spectrometrically both for the large cylinders and for several of the small cylinders. After a period of two years, the sulfur dioxide content of the large cylinders was compared to another group of small cylinders which had been filled at the same time as the previous group of small cylinders. The later analysis was performed by a chemical method involving the oxidation and conversion of sulfur dioxide to sulfuric acid with subsequent titration of the acid. The results (ratios) shown in Table 1 indicate an initial small loss of sulfur dioxide after transfer from the large cylinder to the small cylinder, but no further significant loss after a period of two years.

The apparent randomness of values presumably represents different degrees of reaction of the sulfur dioxide within

the individual cylinders and indicates the necessity for individual calibration of each small cylinder if these are to serve as standard reference materials.

Table 1. Stability of sulfur dioxide mixtures.

Cylinder number	Elapsed time after transferral	
	Ratio of calculated to measured concentration	Ratio of calculated to measured concentration
	5 days	2 years
308	0.92	
281	0.94	
171	0.97	
132		0.97
181		0.93
264		0.95
282		0.93

The question naturally arises as to the stability of the gas in the large cylinder. Obviously, any reaction that might occur in small cylinders could also take place in the large cylinder, although surface-to-volume considerations might influence the quantitative effects. Unfortunately, the mass spectrometric method originally used did not enable the determination of the absolute concentration of sulfur dioxide. However, the contents of the large cylinders were analyzed, titrimetrically, as described above, and these results, in comparison with the mixing data are given in Table 2.

Table 2. Comparison of analytical concentration with mixing data.

Cylinder number	Concentration based on mixing data ppm	Concentration based on analysis ppm
2903180	2020	2050
H 22490	1954	2025

The analytically determined concentration was higher, in each case, than that calculated from the measured partial pressures of the constituents. Because the high values cannot be explained on the basis of reaction with the cylinder, it seems logical to conclude that calculation of concentrations of SO<sub>2</sub> mixtures on the basis of mixing data is not reliable. To confirm this postulate, a new mixture of SO<sub>2</sub>-air was prepared, in which the components were weighed and the partial pressures were measured after each addition. In this case, the concentration by weight was 2096 ppm while the pressure measurements indicated a concentration of 1900 ppm. Evidently, concentrations based on pressure measurements are too low.

The essential conclusion from all of the above is that it should be possible to prepare samples of relatively high concentrations of sulfur dioxide-in-air which after a short period of ageing can be analyzed with a degree of confidence that the results will remain valid for a period of at least two years. Whether or not a method of pre-treatment could be found that would preclude individual calibrations, needs further investigation.

(E. E. Hughes)



#### 4. OZONE STANDARDS

Photochemical oxidant is one of the most important pollutants in urban air. Not only do such constituents have deleterious effects on man and materials but they are the precursors of smog which has both adverse physiological and visibility effects.

Until recently, total oxidants were determined in ambient air for both pollution research and abatement measurements. The advent of specific instrumental methods now makes possible the determination of ozone, the principle photochemical oxidant constituent, and this measurement has become a requirement in air pollution monitoring. This instrumentation needs a source of known ozone concentration for its calibration. This can be provided by an ozone generator which in turn is calibrated with the neutral potassium iodide method.

In order to provide a reliable calibration procedure, and also to evaluate referee methods for photochemical oxidants, NBS is engaged in a program to provide sources of certified ozone output. This program involves not only the determination of the ozone output of each generator, but a study of the parameters which could affect the output. Hodgeson, Stevens, and Martin [5] have constructed a similar ozone source and used it with a Nederbragt chemiluminescent ozone detector and also in a two month field evaluation test in Los Angeles. A number of assembled generators are shown in Figure 1.

The problem of providing an atmosphere of known ozone concentration for direct calibration of ozone analyzers is a difficult one, primarily because of the nature of ozone. Ozone is an extremely reactive oxidant, oxidizing most reducing materials and many organic materials. Ozone is fairly stable at ordinary temperatures but can easily decompose to normal oxygen in contact with solids. Many surfaces promote this change and as a result, only glass, quartz, Teflon and

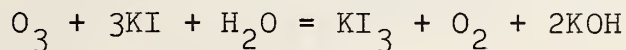




Figure 1. Ozone generators.

mylar can be used in the parts of the generating or detecting system which are in direct contact with ozone. Because of its reactivity, it is very difficult if not impossible to prepare and keep a volume of air of known ozone concentration for any reasonable length of time. Such known concentrations are not only necessary for calibrating instrumental ozone monitors, but also for the study of the stoichiometry of ozone reactions. While it has been assumed for a number of years that there is a 1:1 reaction of ozone and iodine in neutral KI buffer, it has only been in the last two or three years that other methods [6,7,8] have substantiated this because of their 1:1 reaction with ozone. There is at present no "absolute" method available for the determination of ozone.

The neutral potassium iodide method in which ozone reacts with a 1 or 2 percent KI solution in a phosphate buffer of pH 6.8 has been designated the method of choice [9]. This assumes the following reaction:



The  $\text{KI}_3$  is usually determined by spectrophotometry by comparison with known concentrations of iodine in potassium iodide. It is not possible to prepare a container of gas of known ozone concentration, and an alternative is to generate ozone at a steady rate under reproducible conditions. This can be accomplished by passing a known flow of clean dry air through a quartz tube irradiated by ultraviolet light from a low-pressure mercury lamp. The ozone output can be varied by changing the UV intensity irradiating the air stream. The air containing ozone passes to a sampling manifold where a number of samples can be withdrawn simultaneously.

#### A. Design

The actual generator is shown in Figure 2. It consists of an aluminum box containing the ozone source, a UV lamp, and a quartz tube (length 38 cm, OD 2.5 cm) in which dry air is irradiated as it flows through. Covering the lamp is a brass tube with two slots 0.16 cm wide and 180 ° apart, running the length of the tube. The tube is placed so that one slot is directly between the lamp and the irradiation tube. Its purpose is to reduce light intensity and hence the ozone output to an appropriate level. In addition, the inside of the aluminum box is black anodized to reduce internal reflections. This generator provides four ranges of ozone concentrations which can be varied from zero to a maximum. This is accomplished by two methods: First, the UV lamp, lamp base and slotted brass tube are mounted on a circular plate which can be rotated 180° giving two positions for the lamp. In one position, the lamp is ~ 5 cm from the irradiation tube,

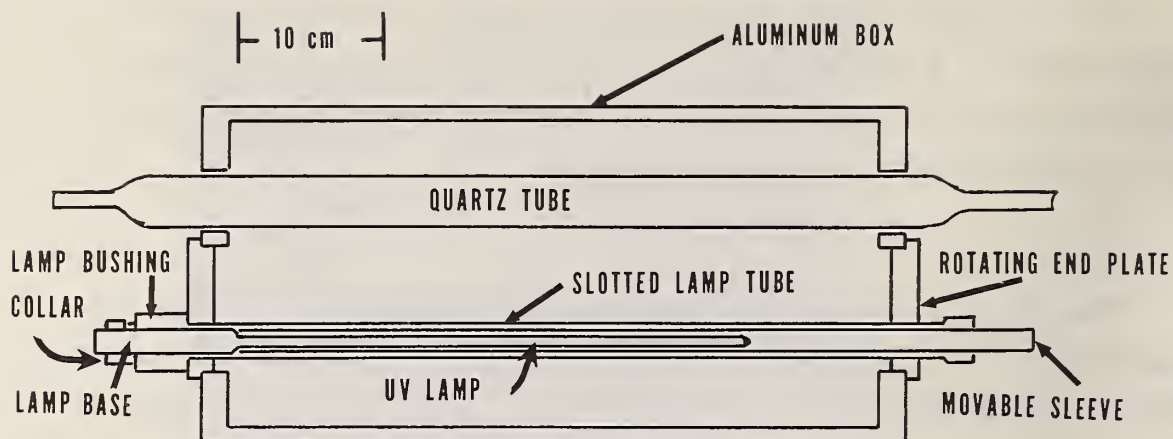


Figure 2. Ozone generator showing principal features.

in the other it is about 2.5 cm. Second, it was found that the cross section of the UV lamps is not circular but elliptical resulting in two positions of maximum intensity,  $180^\circ$  apart. This feature was utilized to give two additional ranges. A pin was placed on the end of the lamp base bushing and a collar was placed on the lamp base. A  $90^\circ$  cutout was made in the collar in such a way that with the pin at one end of the cutout, a maximum output results. Rotating the lamp base to position the pin at the other end of the cutout results in a minimum output. These positions are very reproducible. The four possible ranges produced by combinations of lamp positions are:

	Distance between lamp & tube, cm	Rotation	Range, ppm, at 5 l/min
1	2.5	max	0-0.8
2	2.5	min	0-0.2
3	5.0	max	0-0.25
4	5.0	min	0-0.04

The ranges are only approximate as there is a considerable difference in the output of the lamps. Each range can be varied from zero to the maximum by a movable aluminum sleeve which slides between the lamp and the brass tube. This sleeve is marked in arbitrary units from 0 to 100. At zero, the UV lamp is completely covered and there is no ozone formed. At 100, it is not covered at all and output is at a maximum.

If the lamp intensity were uniform along the long axis, then the output of ozone should be linear between 0 and 100. Analyses showed that between 0 and 10 and 90 and 100 the output tended to vary from linearity. Occasionally other points would not fit the line as well as was desired. This may be because of irregularities in the lamp along its length. Because of the variations in roundness, it is possible that there may also be longitudinal variations which give effects which are difficult to separate from normal analytical uncertainties.

The laboratory air supply at ~20 psi is passed through a silica gel dryer to remove moisture and other impurities. A large wad of glass wool is placed at the end of the drier to remove large particles. The flow is regulated by a needle valve and measured with a mass flow meter. Five l/min is the usual air flow. This meter is easily read to about 0.5 percent. Copper tubing with a few short connections of tygon tubing are used to move the air through the system to the generator. The generator is connected to a sampling manifold by a spherical glass joint and no reactive materials are in the system downstream of the generator. There are seven outlets on the sampling manifold. One is connected with teflon tubing to the Mast meter, which continuously monitors the ozone. Other outlets are used for sampling for the neutral potassium iodide method. A schematic of the entire apparatus is shown in Figure 3.



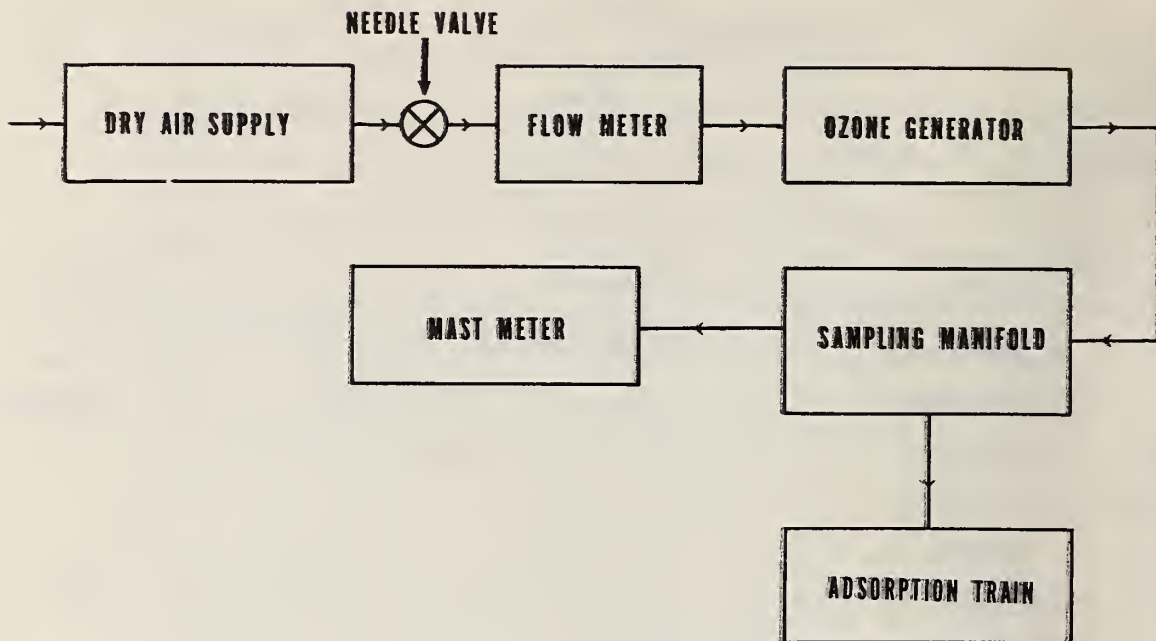


Figure 3. Apparatus for ozone production and analysis.

#### B. Method - General

The dry air passes through the generator and the flow rate is monitored with the flow meter which in turn is checked at least once a day with a wet test meter. If the flow deviates from 5 l/min by more than 1 percent, it is adjusted with the needle valve. Closer adjustment is difficult. Two outlets from the manifold are connected to absorbers with flexible teflon tubing. If two absorption trains are in operation, a maximum of 3.5 l/min will be drawn through them leaving a reserve of 1.5 liters vented out of the manifold.

Two midget impingers in series are used to collect the ozone. These are connected to a vacuum system through a trap, wet test meter, and needle valve, with a three-liter bottle as ballast. The usual sampling rate is 1.5 l/min. The size of sample is determined by the ozone concentration and by the method used. Two chemical methods were employed:



(1) the neutral potassium iodide method [10] and (2) the Bergshoeff variation of it [6]. Between samplings, the sampling system was connected through dummy impingers to maintain equilibrium in the system. Some details of the methods are given below along with comments on their advantages and disadvantages.

### 1. The Neutral Potassium Iodide Method

The method used is essentially that recommended by the Intersociety Committee [10]. Ten ml of the pH 6.8 potassium iodide absorbing solution are used in each of two absorbers. The sample size varied from 30 l to 10 l for the ozone range used (0.03 to 0.25 ppm). At the end of the sampling, each solution was transferred to a 25 ml volumetric flask. Each absorber and the connecting glassware were rinsed with buffer solution which was also added to the flasks, after which the flasks are filled to the mark and mixed. After 30 min, absorbance readings were made, using a spectrophotometer, at 352 nm with 50 mm cells. A calibration curve was prepared using iodine solutions of known concentration. The sampling volume was corrected to 760 mm and 25 °C. Corrections were also made for the water vapor picked up by the dry air in the absorbers and wet test meter. One microequivalent of iodine is equal to 12.72  $\mu$ l of ozone. Under the conditions used here, 2.5  $\mu$ l of ozone forms iodine with an absorbance of about 0.5.

The main problem with this method is the volatility of the iodine and the ease with which it is lost. Higher ozone concentrations at longer sampling times give results that are slightly lower than expected. In general the volume of sample is kept to a practical minimum. Some sensitivity in measurement is sacrificed to avoid iodine losses. We use 25 ml volumetric flasks to obtain more accurately measured solution volumes and 50 mm absorption cells to increase the sensitivity. It is probably better than a measured 10 ml volume in the absorber and 10 mm cells. We followed the

directions of waiting 30 minutes before measuring the absorbance. We confirmed earlier reports [10,11] that the iodine intensity reached a maximum in about 30 minutes and then decreased. Bergshoeff and others [6] have reported that iodine is lost by adsorption on glass. This seems quite likely to be appreciable where there is only 0.2 of a microequivalent or less present.

## 2. Bergshoeff Method

Bergshoeff [6] suggested the addition of a small amount of thiosulfate to neutral buffered potassium iodide. The iodine which is formed by the ozone reacts immediately with the thiosulfate and so cannot be lost by volatilization. A measured amount of iodine, in excess of the amount needed to react with all the thiosulfate even if no ozone is present, is added after sampling, and the excess iodine is then determined spectrophotometrically. Bergshoeff does not give the values of the concentrations. He also uses a special 4-section absorber rather than impingers. We chose our concentrations such that each 10 ml neutral KI absorbing solution contained 0.80 microequivalents of thiosulfate. After sampling and a 30 min wait, the absorbing solution was transferred to a 25 ml volumetric and 5 ml of 0.0002 N iodine solution (1.0 microequivalent) is added. The absorbance is measured at 352 nm using 20 mm cells. A blank (0.8  $\mu$  equiv thiosulfate + 1.0  $\mu$  equiv I) must be measured with each sample. The excess of iodine found in the sample is equivalent to the ozone sampled. A calibration curve is prepared using 0.0002 N iodine solution. Figure 4 is a graphic representation of the procedure.

In the blank the iodine reacts with an equivalent amount of thiosulfate leaving an excess (CD) of  $I_2$  (in this case 0.2  $\mu$ g) which is measured spectrophotometrically. In the sample an amount of ozone (BC) reacts with KI forming iodine which reacts with thiosulfate (BC). When 1.0 microequivalent

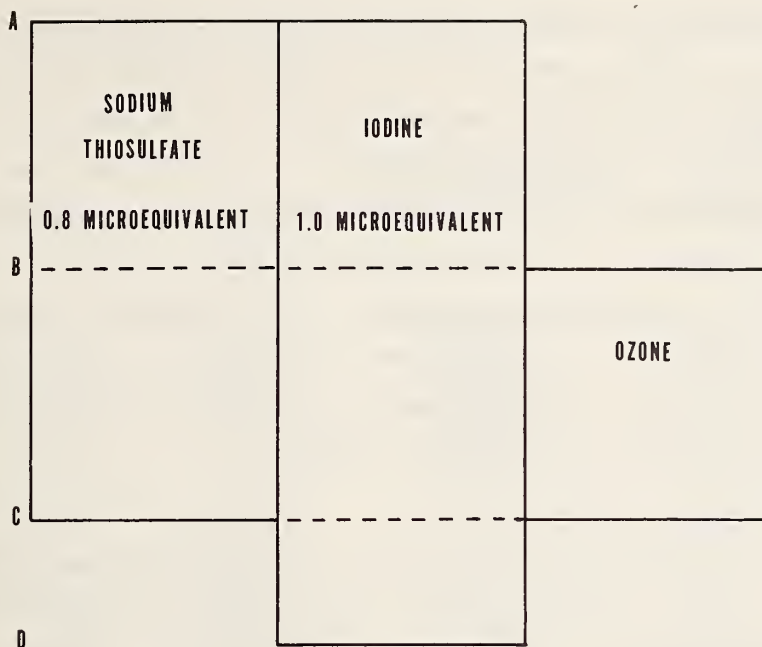


Figure 4. Analytical scheme for Bergshoeff's method.

of iodine (AD) is added, part, (AB) reacts with the remaining thiosulfate leaving BD to be measured. Subtracting the blank CD from this leaves the iodine equivalent to the ozone which was sampled.

The advantage of this method is that there is no loss of volatile iodine during the sampling making it possible to sample for as long as one hour. Two absorbers in series were used for sampling but usually 95 to 99 percent of the total ozone was found in the first absorber. The lower efficiency is associated with lower ozone concentrations. One disadvantage of the method is that many pipetting operations must be performed. Another is that 0.002 N iodine solution changes rather rapidly and loses about 3 percent of its strength in 3 hours. Accordingly, it is necessary to prepare a new solution every 3 hours.



A modification of the Bergshoeff method has been tried. The excess thiosulfate present after sampling is titrated with 0.01 N iodine solution using starch as an indicator. Two ml of 0.001 N thiosulfate is added to each impinger. The titration is carried out in the impinger so no transferring of liquid is necessary. A microburet with a capacity of 1 ml is used for the iodine solution. The method worked very well for the higher concentrations but was not sufficiently precise with low ozone concentrations, mainly because of difficulty in determining the end point.

### 3. Mast Ozone Meter

All of the chemical measurements of ozone were simultaneously compared with measurements using a Mast oxidant analyzer. The average efficiency of the Mast analyzer was found to be 85 percent. The analyzer is satisfactory for quickly following the output of the generator, and for setting the generator at a desired concentration. There is a variation in the signal of the Mast meter which may at times be as large as 0.5 mV per hour which is equivalent to 0.005 ppm ozone. In the Intersociety method on the continuous monitoring of oxidant [12], it is stated that the hourly variation should not exceed  $\pm 0.01$  ppm.

### C. Results of Calibration

Table 3 is a summary of the calibration of twelve generators, obtained by a least squares fit of the data. The determinations were made at sleeve settings which would give ozone concentrations of approximately 0.04, 0.08, 0.12 and 0.20 ppm. Ozone determinations were made at each setting by both methods with at least four determinations for each setting and at least 16 for each generator. The slope of the line of concentration in ppm vs. sleeve setting is given in column 2 and the intercept is given in column 3. The predicted ozone concentration for any setting is given by  $O_3$  (ppm) =  $AX + B$  where X indicates the sleeve setting.

Table 3. Summary of calibration analyses of twelve ozone generators.

Generator number	Slope A	Intercept B	Standard deviation of the slope	Standard deviation of the predicted values (ppm)	
				Ends	Middle
1	.00237	-.0136	.000042	.0018	.0011
2	.00294	-.0101	.000069	.0025	.0018
3	.00241	-.0008	.000052	.0021	.0012
4	.00329	-.0126	.000069	.0024	.0015
5	.00297	-.0182	.000058	.0026	.0016
6	.00292	-.0182	.000086	.0030	.0018
7	.00209	-.0081	.000035	.0015	.0009
8	.00224	-.0167	.000044	.0018	.0012
9	.00229	-.0035	.000030	.0012	.0007
10	.00249	-.0128	.000048	.0018	.0012
11	.00259	-.0109	.000044	.0021	.0010
12	.00326	-.0240	.000057	.0019	.0011

The uncertainty of the predicted value of the ozone concentration for these generators is of special interest. In this kind of fit, the uncertainty is greater at the ends and smaller in the middle. The average of the standard deviation of the ends of the line is given in column 5 while the standard deviation in the center is given in column 6.

The results show a large variation both in the slope and in the uncertainties. The variation in the slope is undoubtedly due to differences in the UV lamps, especially in the thickness and shape of the quartz envelope. These variations were expected. An examination of the lamp output using a photocell while seeking the maximum and minimum positions had shown large differences in the lamps. The variations in the standard deviation of the predicted values



are probably due to the analytical method. It is possible that there are some changes in the ozone output, due to variations in lamp output or the flow through the irradiation tube, but those would be very small compared with the uncertainties in the analytical method.

To check on the reproducibility of the method, 21 determinations were made at the same generator setting over a period of three days. The standard deviation of a single measurement was 0.004 ppm and the 95 percent confidence limit for the mean was  $0.0896 \pm .0017$  ppm.

For most of the generators, a set of simultaneous determinations were made by the two KI methods. As was expected, the Bergshoeff method gave slightly higher results. Averaged results are given in Table 4.

Table 4. Differences found between neutral potassium iodide method and the Bergshoeff method.

Ozone level	Average Difference between methods
0.20 ppm	.006 ppm
0.12	.003
0.08	.002
0.04	.001

These differences do not appear to be significant and so the results were pooled in the calibration curve.

Early work showed that results deviated markedly from a straight line near the ends of the lamp, that is with high and low sleeve settings. This could be caused by a different geometry of the position of lamp slot and tube, especially at the low setting, where only the UV rays which are perpendicular to the lamp and tube can produce ozone. It could also be due to changes in the quartz lamp envelope near either end.

#### D. Stability

In investigating the stability of the generators, we have looked for both long and short term changes in the output.

Hodgeson, Stevens and Martin [5] found that the output of their generator decayed about 15 percent in the first two weeks of use. We were interested in whether this decay was greatest during the first few hours of use, or was uniform during the entire two weeks. Accordingly the ozone output of most of the generators was measured during the first two hours of use by both the neutral KI method and the Mast meter and was again measured after 48 to 72 hours. Any change which might have occurred was hidden by an unexpectedly long warm-up period. A generator would rise to about 80 percent of its maximum output within 30 min after it was turned on and would remain relatively constant for anywhere from 2 to 12 hours before increasing. A lamp which has been off only an hour will reach its maximum within 5 min, but for much longer than that an overnight warm-up is the most satisfactory procedure. This slow warm-up apparently is involved with the vaporization of the mercury of the lamp. A UV lamp which had not been used for several days was removed and gently heated in a flame. It then reached about 95 percent of its maximum output within a few minutes but required about two hours to reach the maximum. This suggests that a warm-up of the entire box may be involved. One generator was wrapped in heating tape and the temperature raised while following the ozone output. As the temperature increased within the box, the ozone output decreased. With a rise of 15 °C within the box, there was a 5 percent decrease in output.

On the possibility that the voltage regulator or the transformer might also need a warm-up period, they were turned on overnight and then used with a cold lamp. This resulted in a lower level of ozone production for several hours. In addition the voltage on the lamp was measured.

This was found to reach a steady state within 15 min. For most generators the voltage on the lamp was 410 volts. A few were as high as 420 volts.

Mast analyzer readings appeared to indicate short term (one or two hours) changes at times as high as 4 or 5 percent. Such changes could not be verified by the neutral KI measurements as the normal variations in the method approached this value. At other times the Mast meter would run for hours with variations of less than one percent. It was also noticed that the variations were relatively higher at high ozone concentrations. It is believed that the short time changes as indicated by the Mast meter are in fact variations within the Mast meter and not variations occurring in the ozone generator. The planned use of a chemiluminescent ozone meter with its rapid response time should be helpful in determining whether or not variations arise from the generators.

The long-time rate of decay of the generators is also of special interest. Two of the generators have been in use for extended periods of time. The ozone outputs for a selected calibration point are shown in Tables 5 and 6. Both generators show a similar decreased output with time. The decrease is essentially linear and is about 1.3 percent per 100 hours in each case.

Table 5. Generator Number 6. Change of ozone output with time.

Hours of use	Ozone output, ppm
120	.200
144	.200
216	.200
500	.191
524	.194
548	.189

Table 6. Generator Number 9. Change of ozone output with time.

Hours of use	Ozone output, ppm
120	.207
144	.210
265	.199
290	.191
314	.199
725	.190
773	.191
777	.186
821	.186

An earlier model of the ozone generator showed a decrease of 18 percent in 1080 hours or a slightly higher decrease of 1.7 percent per 100 hours. In general the decrease of output of a generator will be about 1.5 percent per 100 hours of use. This decrease which has been noted by others is probably caused by solarization of the quartz of the lamp envelope.

A number of factors were examined to determine if they had any effect on the ozone output or analysis. Dry air was used in the generator. Saturation of the incoming air with water vapor decreased the ozone output by about 20 percent. The quartz irradiation tube was rotated and moved back and forth within the box. No change in ozone output was noted.

Thirty feet of smooth teflon tubing was used to carry the ozone from the manifold to the Mast analyzer. After a few minutes there was no difference in readings from that of ozonized air carried through the usual three feet of tubing.

(R. A. Paulson, W. D. Kinard, E. E. Hughes)



## 5. NITROGEN DIOXIDE STANDARDS

Nitrogen dioxide permeation tubes have been studied in great detail in order to assess their potential as standard reference materials similar to the sulfur dioxide permeation tube standards (SRM 1625, 1626, 1627). However, many more problems are associated with these devices and the ultimate practicality has not yet been fully evaluated.

A number of commercially available nitrogen dioxide permeation tubes were obtained. The permeation rates were determined by a gravimetric method over the entire lifetime of the tubes. The most significant result of this study is the observation of a steadily declining rate with time. A typical result from a single tube is shown in Figure 5. This tube was maintained in a dry atmosphere at a fixed temperature during the period in which the gravimetric determination of the weight loss was performed.

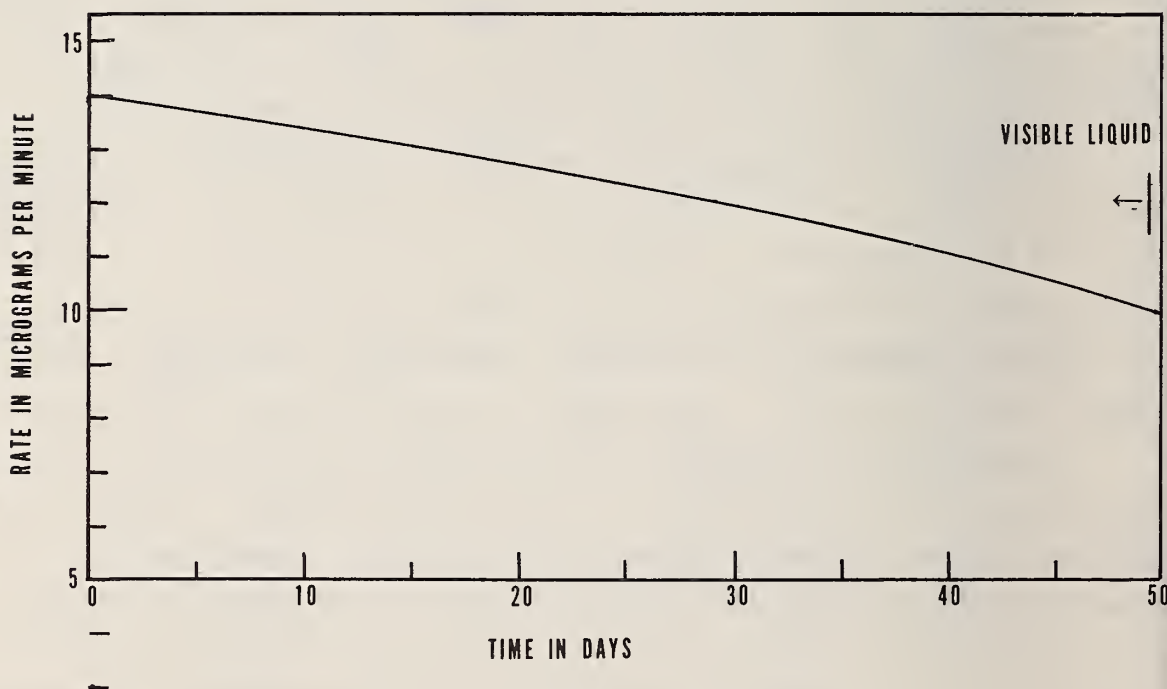


Figure 5. Rates for commercial nitrogen dioxide permeation tubes.

After the disappearance of the liquid phase of nitrogen dioxide, a few small droplets of liquid were observed within the tubes. The color of the vapor and liquid within the tube suggested that the droplets were not nitrogen dioxide but rather some other material. A small amount was removed and was analyzed mass spectrometrically. The spectrum consisted of a large peak due to water and smaller peaks due to nitrogen dioxide, a spectrum similar to that obtained from fuming nitric acid. The substance was probably nitric acid and dissolved nitrogen dioxide. The quantity of water was considered to be much greater than could have effused into the tube between the time it was manufactured and the time when the last visible amount of nitrogen dioxide disappeared. This suggested the strong possibility that the water had been present in the nitrogen dioxide with which the tube was originally charged.

Two solutions to the problem of declining rate were suggested, either removal of the water from the nitrogen dioxide before filling the tube, or inclusion of a drying agent in the tube to remove water originally present and any water which subsequently effused into the tube. Mechanical problems associated with drying the nitrogen dioxide were considered to be greater than those involved in including a drying agent within the tube and this approach was tried first.

A number of tubes were prepared in which a small amount of phosphorous pentoxide was included in addition to the nitrogen dioxide. The rates of these tubes were determined gravimetrically during the entire period when a weight loss was occurring. The results for a typical tube are shown in Figure 6. It was presumed that the loss in weight was due to nitrogen dioxide and the further presumption was made that this technique would result in a tube sufficiently stable for use as a standard reference material. Tubes of this type were later used by several different groups in field studies and some question arose as to the composition of the material permeating through the tube. At present it appears that a

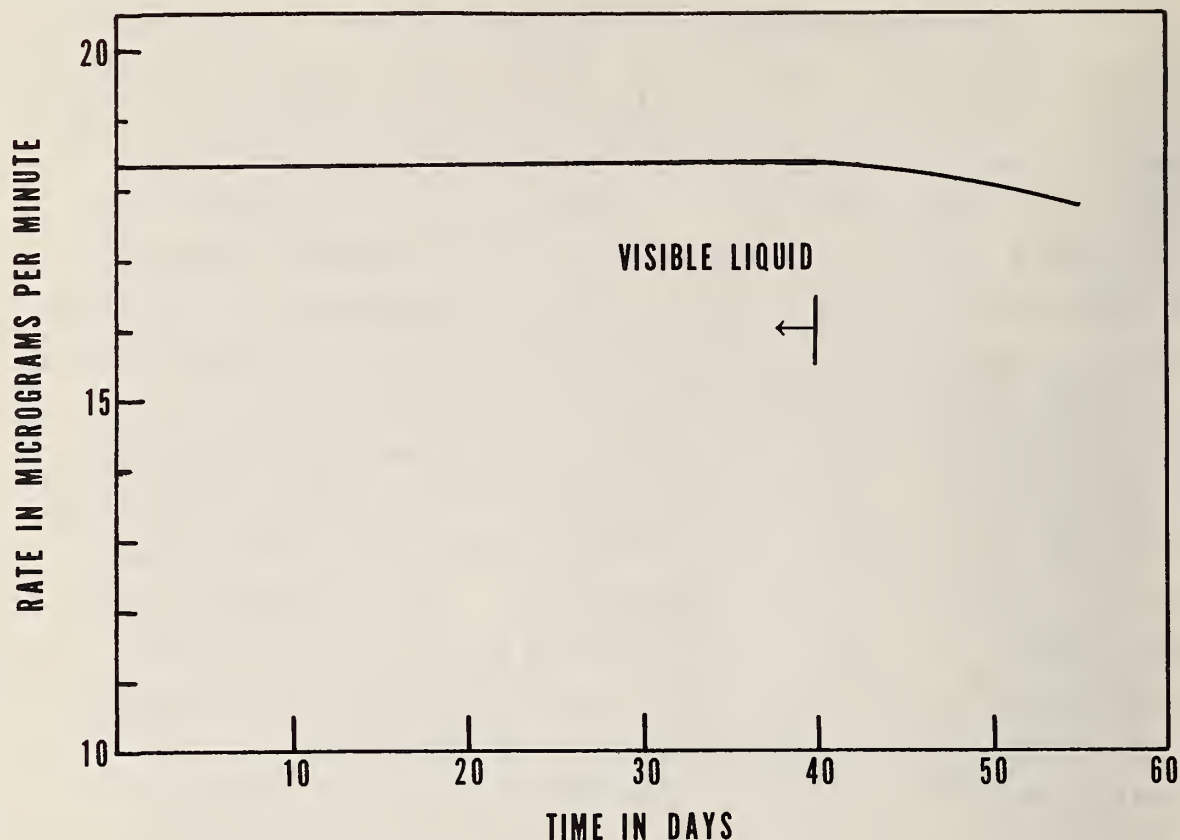


Figure 6. Rates for nitrogen dioxide tubes containing a drying agent.

portion of the vapor is nitric oxide. The amount effusing is apparently constant for a tube, but quantities of 1 to 6 percent have been estimated for different tubes. This aspect of the problem is being studied further and a possible explanation may be found in the total system which includes at least water, nitrogen oxides, phosphorous pentoxide and phosphoric acid.

Phosphorous pentoxide is reported to react with nitrogen tetroxide to give a compound of empirical formula,  $P_2O_5 \cdot 2NO$  and oxygen [13,14]. The reaction is extremely slow at room temperature and would not affect the rate of permeation of nitrogen dioxide through Teflon. The compound,  $P_2O_5 \cdot 2NO$ , can, however, react with water to yield phosphoric acid and nitric oxide.

While water appeared to be the principal reason for a declining rate, other possibilities relating to changes in the physical or chemical nature of the tube material were considered. It had been observed early in the development of these tubes that small blisters appeared on the surface after a short period of time [15]. The blisters appear to be a few micrometers in diameter and are found only on the outer surface. Microscopic examination of cross sections of tube material obtained from badly blistered tubes failed to disclose evidence of any changes other than on the surface. A crude but definitive experiment was performed which consisted of refilling tubes which had shown a significant change in rate during one lifetime. The rates after refilling were determined and compared to those before. If the change in rates were due either to a reaction between nitrogen dioxide and the tube material or to a change in structure of the Teflon then the rate after refilling should have been the same as the last measured rate before refilling. This was not the case, however, and the initial rates after refilling were approximately the same as those which would have prevailed when the tubes were originally filled.

Nitrogen dioxide permeates through Teflon tubing at an undesirably fast rate. Permeation tubes constructed to dimensions similar to sulfur dioxide permeation tubes produce quantities of nitrogen dioxide that are inconveniently high for dilution to ambient atmospheric levels. In practice, the shortest tube which can be filled is 2 cm. Furthermore, because of the high rate, the life of a tube is only two or three months. Other devices were needed which would both extend the life of the calibrant, as well as, produce smaller quantities of nitrogen dioxide. A further requirement of such devices is that the final rate be predictable to some extent from the dimension of the component parts in order to avoid the necessity of producing large numbers of devices to satisfy the needs for a few rates. Two relatively simple



devices were designed and built both of which have been preliminarily evaluated and both of which appear to be satisfactory.

The first, shown in Figure 7 consists of a disk of TFE Teflon forced into the end of a glass tube. The last inch of the tube is shrunk slightly around a carbon mandrel and the end is heated to form a constricting lip. The disk is machined for a snug fit in the larger diameter. The disk is then forced into the constriction, while the tube is gently heated. The tube is then partially filled with liquid nitrogen dioxide, cooled, partially evacuated, and sealed. This device can be constructed to yield rates of any value up to about  $0.1 \mu\text{g}/\text{min}$ . Higher rates require a disk which is too thin to form a tight seal to the glass.

A second device with which rates between  $0.1 \mu\text{g}/\text{min}$  and the rates produced with 2 cm tubes, is shown in Figure 8. Glass tubing of slightly larger diameter than the inner diameter of the Teflon tubing is forced into a short length of glass tubing. A plug is seated in the teflon and a stainless steel or brass fitting is swaged around the tube. The final rates can be controlled to some extent by controlling the distance between the end plug and the glass tubing. The tube is filled with nitrogen dioxide and sealed in the same manner as previously described.

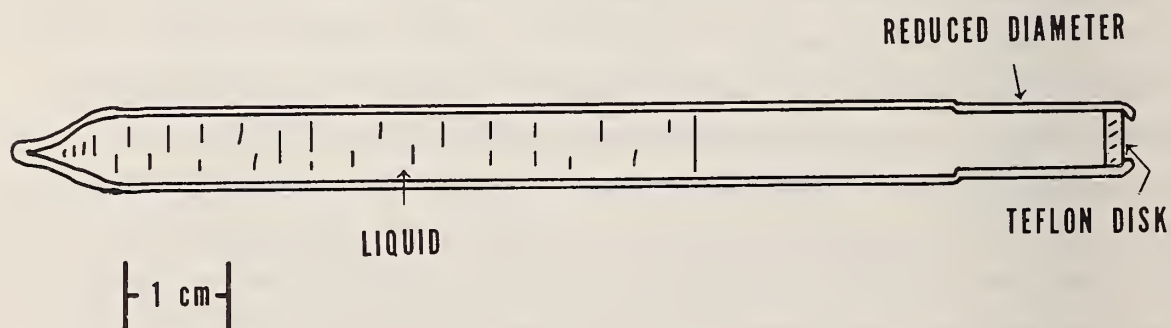


Figure 7. Device with very low permeation rate.

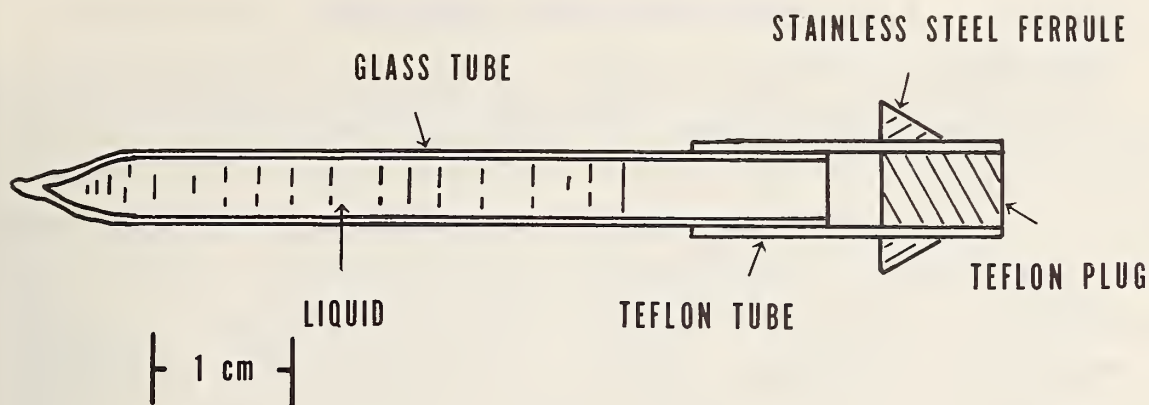
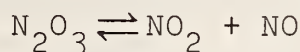
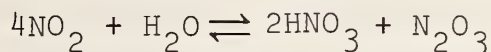


Figure 8. Device with intermediate permeation rate.

Some of these tubes have been fabricated with a small amount of phosphorous pentoxide inside but the majority have not been made in this way. These devices have potential lifetimes of up to three years. If the initial charge of nitrogen dioxide is relatively dry, then the effect of water on the rate will be insignificant for a rather long period. The amount of water which will effuse into a tube during normal use and while observing reasonable precautions regarding exposure to moist air will be insignificant. Consequently, until the effect of phosphorous pentoxide and the products resulting from the use of drying agents is known, tubes and other devices will be prepared using dried nitrogen dioxide.

Nitrogen dioxide reacts with water as follows:



The compound,  $\text{N}_2\text{O}_3$ , is green, and "wet" nitrogen dioxide initially exhibits a color best described as greenish brown which after standing becomes the brown typical of nitrogen dioxide. An attempt will be made to measure the apparent water content of freshly prepared devices by measurement of the color assuming that the spectral characteristic of a mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_3$  differs from that of  $\text{NO}_2$ .

(E. E. Hughes)

## 6. CARBON MONOXIDE STANDARDS

Investigation of the analysis and storage of carbon monoxide in air mixtures have defined the conditions necessary to produce an SRM in the 10-1000 ppm range. This SRM could be certified to about  $\pm$  2-3 percent of the stated concentrations. As previously noted [16], there is no evidence of loss of carbon monoxide from mixtures when stored in stainless steel cylinders at 60 °C for two weeks. Further aging tests of six weeks duration at 60 °C of two stainless steel cylinders containing 6.5 ppm carbon monoxide in air indicated no loss of carbon monoxide. In contrast, the carbon monoxide concentration of an 8.5 ppm carbon monoxide-in-air mixture stored in a mild steel cylinder at 60 °C for about one week decreased to 4.5 ppm. The carbon monoxide was determined by catalytic conversion to methane [1] and by subsequent comparison with methane in air standards.

The instrumental parameters which give optimum separation of carbon monoxide and methane on the molecular sieve column and optimum conversion of carbon monoxide to methane on the nickel catalyst are as follows:

Catalyst temperature - 450 °C

Hydrogen flow to nickel catalyst - 25 cc/min

Column temperature - 85 °C

Hydrogen flow through column - 90 cc/min

Good peak separation is assured if the molecular sieve column is pre-conditioned by passing helium through it at the rate of 100 cc/min for 12 hours, at 300 °C. This permits the use of the flow rates for helium and hydrogen given above, which are higher than the previously recommended values.

The apparatus described earlier [1] was modified so that hydrogen could be introduced into the helium carrier gas stream just ahead of the nickel catalyst, instead of being mixed with the helium carrier before its entrance into the molecular sieve column.

A series of carbon monoxide in air mixtures was prepared in stainless steel cylinders in order to study the stability of such mixtures at room temperature. The results are given in Table 7.

Table 7. Stability of carbon monoxide mixtures.

Cylinder number	Carbon monoxide concentration, ppm by volume			
	Calculated from pressure data	From analysis	From analysis	From analysis
	1-71	1-71	2-71	4-71
2X	92.3	89.9	89.9	88.9
33S	101	90.7	92.5	93.1
2Z	17.4	16.7	16.7	16.7
40S	16.5	15.9	15.9	15.6
1	941	896	886	---
100	941	890	889	879

These results indicate that there was no loss of carbon monoxide within the limits of experimental error ( $\pm 2-3$  percent). However, the concentrations based on analysis average about 5 percent below the concentration calculated from the pressure measurements during mixing. This is due to the incomplete reduction of carbon monoxide to methane over the nickel catalyst. This reaction appears to be about 95 percent efficient at best.

A nickel catalyst (catalyst I) prepared according to the method of Stevens [17], but without using a fluidizer for evaporation of the water gave the same results as a catalyst (catalyst II) prepared as above but using a fluidizer. These results are shown in Table 8. No change in conversion efficiency was observed when the catalyst temperature was varied over the range of 320 to 510 °C.

Analysis of mixtures of carbon monoxide in air for use as SRM's will be based on comparison of the SRM material with laboratory standards prepared by gravimetric measurements of the carbon monoxide and air. Uncertainties in the analysis due to catalyst inefficiency will be eliminated by this method.



Table 8. Comparison of catalyst performance.

Sample number	Carbon monoxide concentration, ppm by volume		
	Calculated from pressure data	From analysis catalyst I	From analysis catalyst II
1	941	879	887
2	1080	1028	1022

Similarly, the use of SRM's as calibration standards would eliminate such an uncertainty when using the same analytical method for air pollution measurements. Both the laboratory standards and the SRM's will be prepared and stored in stainless steel cylinders.

(E. E. Hughes, J. M. Ives)

## 7. PARTICULATE STANDARDS

### A. General Considerations

The chemical composition of the particulate constituents of the atmosphere is becoming of increasing interest. While present ambient air standards consider only the mass concentration of total particulates, emission standards for stationary and mobile sources are being developed for hazardous metals and asbestos, and standards for other constituents will no doubt be established.

While analytical data are being collected and reported on various constituents of atmospheric particulates, there is presently no way to evaluate their reliability. Likewise there is no supply of material available for use in checking new methodology, to permit interlaboratory evaluations of referee methods, and to provide analytical control of measurement systems or networks.

To improve the situation described above, to advance the state of the art of particulate analysis, and to provide a medium for the exchange of analytical techniques and methodology, the National Bureau of Standards proposes to issue a particulate matter reference material. This material will be a large sample or samples of urban atmospheric particulate matter which will be carefully mixed to provide maximum uniformity of composition. It will be exhaustively analyzed and issued with a certificate of analysis, indicating the limits of analytical uncertainty.

The objective is to achieve a "complete" analysis of the material. In this framework, the "not-determined" category will be kept to a minimum and its constituents will be determined in the future, as possible. Users of the material will be encouraged to report their findings about its composition. Such information will be used to supplement and up-date the compositional characterization of the material.

A major problem, up to the present time, has been to obtain a satisfactory material. A satisfactory material should be a

typical urban particulate material, collected in such a manner as not to distort its composition. It should be collected over a reasonably short period of time so that large seasonal changes in composition would not occur during sampling. At least 10 pounds and preferably 100 pounds of material are required.

Several candidate materials have been examined and rejected for such reasons as: excessive content of filter fragments; large proportions of insect parts; non-representative composition, *e.g.* fly ash. The most desirable sample presently appears to be one collected by a bag-house filter. After several cycles of operation, the material removed after each cycle should be representative of that collected during the cycling period. In other words, little filter hold-up would be expected. Such a method of collection appears to require the construction of an expensive, special sampling apparatus. There are probably other ways in which a sample of required characteristics could be collected and suggestions in this respect would be welcomed.

#### B. Feasibility Studies

A small sample, amounting to 100 g of material, was furnished to us by Dr. Richard Thompson, of EPA, for feasibility studies. This material originally came from the filter of a large building in New York City. A number of competences in the Analytical Chemistry Division have examined and analyzed this material. While it is not deemed to be entirely satisfactory as a reference material, even if available in large quantities, it appears that the concept is valid and that many valuable analytical properties could be certified on a suitable particulate material.

The results of the various investigations will be reported in several Progress Reports of the Sections in which the work was done. The studies made in the Microchemical Analysis Section are reported in the following.

## C. Microchemical Investigations

### 1. General Appearance

The sample is a dark gray dust, fairly uniform in appearance. The dust looks sticky or oily and some portions are matted together. There are a number of larger pieces of material which can be identified by eye but on the whole the percentage of these is rather small. Some of the things which can be seen are pieces of paper, fragments of leaves, pieces of string or thread, plant fragments, and flat chips of paint. No insects or insect parts are seen.

The material which R. Brady (Section 310.07) had extracted with water and benzene was also examined. This was no longer "sticky". There was a practical separation of the particles and fibers in that the fibers had matted together and many of the particles had been shaken from the fibers.

### 2. Microscopic Examination

Under reflected light, the sample is grayish brown and appears to be a mass of fibers and particles. Almost all the fibers are less than 1  $\mu$ m in length. The particles range in size from 200  $\mu$ m down to less than 1  $\mu$ m. Most of them appear to be 10  $\mu$ m or less. There are some conglomerates but they seem to break up easily when the sample is dispersed in immersion oil or other media. Very conspicuous components of the dust are black spheres up to about 200  $\mu$ m in diameter. These are oil-soot spheres and will be discussed later, under transmitted light. A large portion of the particles are opaque.

a. Fibers. As mentioned before, most of the fibers are short--1  $\mu$ m or less. A large portion of these, about two-thirds, appear to be wood fibers which have probably come from paper. These fibers are mostly long flat tapering cells with some nodes. These show first order gray and white colors for the most part, and show parallel extinction. There are also the flat baggy cells typical of nonconiferous wood pulp. The appearance of these fibers is similar to those in several of the larger



pieces of paper found in this sample and which look like a filter paper. This might indicate that the bulk of the fibers in the dust actually came from the filter and not from the atmosphere. However, we do not know what kind of filter or filtration was used. It could be a bag filter or an electrostatic precipitator. It is doubtful that it is fiber glass, as glass fibers are rather scarce in the sample. Other fibers present are cotton, wool, rayon and nylon. Most of these are dyed.

A few fine animal hairs are seen and a few glass fibers are also seen. These are approximately 5  $\mu\text{m}$  in diameter and 100 to 200  $\mu\text{m}$  long. Asbestos fibers were not seen although they were looked for especially.

b. Combustion Products. These make up a large part of the particulate matter in the sample and range in size from several hundred  $\mu\text{m}$  down to submicron size. The most conspicuous materials are the oil-soot spheres, which range in size from less than 50  $\mu\text{m}$  to about 200  $\mu\text{m}$ . They are black with a rough surface. Some are fairly solid, some are just shells, and some are hardly more than a net of carbon. This is a characteristic of oil-soot spheres and depends on the length of time they are in the hot zone of the furnace and on the amount of air present. All are fairly easy to crush by pushing on the cover slip. Oil-soot is also present as opaque, black irregularly shaped pieces.

Fly ash particles are also present. These are also spheres and vary in size from a few  $\mu\text{m}$  to about a hundred  $\mu\text{m}$  and in color from colorless to black. Some of the larger black fly ash spheres look somewhat like the oil-soot spheres, but they are smoother and more regular in shape and are hard. Often they are magnetic.

Some incinerator products can also be seen. The most noticable are partially burned pieces of wood or paper. They are usually a reddish brown color and semi-transparent. Some of the wood cell markings can be seen.

c. Minerals. Under crossed polars a large number of small anisotropic materials of a crystalline nature can be seen. However, they probably do not comprise more than 5 percent of the sample. Larger pieces are also visible. Of these quartz is the most prevalent and pieces up to 150  $\mu$ m are seen. Other materials seen and identified were iron rust (hematite), glass, and mica or limestone. There were also other crystals, some quite regular in shape, which could not be quickly identified.

d. Biological Constituents. A few pollen grains are seen. They look old and can not be identified without staining. Some spores are also seen but the only one identified is the rather common *Alternaria*. Some plant hairs (Trichomes) are seen as well as fragments from plants. No recognizable insect parts appear to be present.

e. Other. There is an appreciable number of flat, gray, opaque particles which look like paint chips. These are similar to the larger ones picked from the material. Ignition and solubility tests indicate that this material is probably a lacquer.

### 3. Chemical Analysis

Chemical analysis for various metallic elements were undertaken by several of the competences of this Division as was a preliminary characterization of the organic constituents. Deter-

Table 9. Analysis of particulate material.

<u>Determined</u>	<u>Concentration, percent</u>
carbon	23.6
hydrogen	2.2
nitrogen	1.1
ash	60.0
moisture	3.0
sulfate	6.0 <sup>a</sup>
chlorine	1.4 <sup>a</sup>
ammonia	0.7
nitrate	0.4
not determined	9.0

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<sup>a</sup>Included in ash.

mination of several anions and several miscellaneous determinations were made in this Section. The methods employed were essentially conventional procedures and will not be detailed here, because of the preliminary nature of the determinations. However, the results are tabulated for illustrative purposes in Table 9. Much of the "not determined" is believed to be oxygen combined in the organic material present.

Analytical work is continuing on this material with the objective of developing methodology for analysis of the proposed reference standard. This and other work on the sample will be reported in more detail elsewhere.

(R. A. Paulson, J. K. Taylor)

## 8. MICROCHEMICAL ANALYSIS

Analytical support has been provided to a number of projects within the NBS, during the past year. This has consisted of utilizing classical micro- or semimicro-chemical techniques on such diverse materials as flame-retardant fabrics, freeze-dried samples of biological sera, and a wide variety of standard reference materials. Some of the more interesting analytical problems are summarized in the following sections of this report.

### A. Residual and Distillate Fuel Oil SRM's

Combustion of fuels accounts for more than three-fourths of the sulfur oxides emitted into the atmosphere. Accordingly, the limitation of the sulfur content of various fuels is one of the most important techniques for air pollution control. Most of the analytical techniques presently used require a material of known sulfur content for their standardization. Because of the large tonnage of fuels consumed, even a small analytical error could result in large uncertainties in sulfur emissions or undue costs in sulfur removal operations.

As part of the NBS program in the air quality area, two fuel oils, certified for their sulfur content were issued in 1970. These are identified as SRM 1621 Residual Fuel Oil, S = 1.05 percent, and SRM 1622 Residual Fuel Oil, S = 2.14 percent. The analytical work leading to their certification was reported in NBS Technical Note 455 [18]. Because the permissible levels of sulfur are being lowered in many regions, a Residual Fuel Oil, SRM 1623, S = 0.268 percent, and a Distillate Fuel Oil, SRM 1624, S = 0.211 percent, have been added to this series.

The oils for these SRMs were obtained from commercial sources, hence are representative of fuels in common use.

Three samples from each of two five-gallon cans were taken for analysis of each SRM. Each of the six bottles so taken were analyzed for sulfur in duplicate in random order. The analytical method used was essentially that described previously [18], which is a slight modification of ASTM Method D129. One-gram



samples of the oil were combusted in the Parr Oxygen Bomb. Any iron present was precipitated with ammonium hydroxide and filtered before precipitation of the sulfate with barium. Because the sulfur contents were low and the capacity of the bomb was limited to a 1 g sample, the washings from two combustions were combined for each determination. No inhomogeneity was detected between bottles, and the results of the twelve determinations for each SRM were combined. The analytical determinations are summarized in Table 10.

Table 10. Analysis of fuel oils.

Sample SRM No. 1623 residual fuel oil	
Sulfur	0.268%
	$s = 0.0057$
	$n = 12$
	95% Confidence limit = $\pm 0.0035$
Carbon	87.4%
Hydrogen	12.0%
Water	Not detected ( $<0.1\%$ )
Sediment	0.00%
Ash	Not detected ( $<0.005\%$ )

Sample SRM No. 1624 distillate fuel oil	
Sulfur	0.211%
	$s = 0.0071$
	$n = 12$
	95% Confidence limit = $\pm 0.0044$
Carbon	86.6%
Hydrogen	12.5%
Water	Not detected ( $<0.1\%$ )
Sediment	0.00%
Ash	Not detected ( $<0.005\%$ )

Tests were made to determine the loss of volatile constituents. Approximately 10 grams of oil were placed in weighing bottles and allowed to stand open at room temperature. The results are shown in Table 11. The volatility found was not unexpected and does not constitute a serious analytical problem under normal conditions of use. However, significant changes in composition could result from the improper practice of storage of an unstoppered bottle. Accordingly, the user is cautioned to observe the good practice of keeping the bottle stoppered at all times except when actually withdrawing a sample.

Table 11. Volatility of fuel oil SRM's.

Period of exposure	Percent loss	
	SRM 1623	SRM 1624
1 day	0.67	0.73
2 days	0.95	1.19
4 days	1.61	2.10
8 days	2.36	3.40

#### B. Proposed Bovine Liver SRM

A project has been initiated to issue a sample of dried bovine liver as a trace element standard. A large quantity of such material has been prepared and its homogeneity tested. Certification analysis will be undertaken during the current year.

Determinations were made of the nitrogen content of selected samples of this material as one means of homogeneity evaluation. A semimicro Kjeldahl method was used on 300 mg samples. The material had been received from the processor in 25 bottles which were said to be all from the same batch. Five of these bottles were randomly selected for analysis. The nitrogen contents, consisting of the averages of duplicate determinations are summarized in Table 12. A high degree of homogeneity is indicated.

Table 12. Nitrogen content of bovine liver.

Bottle number	Percent nitrogen
23	10.62
3	10.62
13	10.60
12	10.63
5	10.63

C. Metallo-Organic Chromium Compound SRM 1078b

A commercial lot of the metallo-chromium compound, tris(1-phenyl-1,3-butanediono)chromium (III), intended as a renewal of SRM 1078a, was analyzed for its chromium content. The purpose of this SRM is for use in the preparation of calibrants for engine wear monitoring.

The material was received from the manufacturer in four bottles, each containing 2.5 kg of the compound. Bottle No. 1 differed somewhat in appearance and had a distinctly different residual odor and preliminary analysis confirmed that the contents had a different composition from that of the other three. Accordingly, it was excluded from the scheme for certification analysis. Four samples were randomly selected from the remaining three bottles and these were analyzed in sets of 6. Unfortunately, Sample 2B was ruined in the course of the analysis.

The SRM was analyzed by digesting 0.8 g samples in a mixture of sulfuric and nitric acids and fuming off the nitric acid. One milliliter of 60 percent perchloric acid was added and heated to dense fumes to insure complete digestion. The sample was diluted with water and oxidized with ammonium persulfate in the presence of silver ion. The excess persulfate was boiled off and dilute hydrochloric acid was added to reduce any manganese present and take the silver out of solution. The excess chlorine was boiled off and the resulting  $\text{Cr}^{+6}$  solution was titrated potentiometrically with  $\text{Fe}^{+2}$  to a potential break

which occurred around +0.75 mV. The ferrous ammonium sulfate solution was standardized at the beginning of each set of titrations against weighed samples of NBS SRM 136b potassium dichromate. The agreement of duplicate standardizations was better than 3 parts in  $10^4$  each day.

As a check of the method, three samples of SRM 1078a (chromium-organic standard) were analyzed using the above procedure. Values obtained for chromium were 9.75 percent, 9.76 percent, and 9.75 percent, which compare favorably with the reported value of 9.7 percent. In preliminary work, samples of 1078b were analyzed by the above method but omitting the perchloric acid step in the digestion. It was found to be impossible to totally destroy the organic material and therefore, complete oxidation of the chromium was not obtained. This incomplete oxidation was indicated by an inability to maintain a permanganic color in the solutions after the oxidation step.

The value of the standard deviation,  $s$ , is consistent with the expected uncertainty of the analysis, so that a high degree of homogeneity is indicated. The overall average value based on 11 degrees of freedom is  $9.518 \pm 0.007$  where the uncertainty represents the half width of the 95 percent confidence interval. The results of the analysis are summarized in Table 13.

#### D. O-Bromobenzoic Acid SRM 2142

A sample of o-bromobenzoic acid which had been prepared and purified by Mr. C. W. Stanley of the Office of Standard Reference Materials was analyzed and certified as SRM 2142 for use as a microchemical standard in the determination of bromine in organic compounds as well as a standard for carbon and hydrogen microanalyses. The material was subdivided into 12 bottles. Six of these were randomly selected for certification analysis.



Table 13. Chromium content of SRM 1078b.

Bottle	Sample	Order <sup>a</sup> of Analysis	Percent Chromium
2	A	2	9.514
	C	9	9.539
	D	5	9.510
3	A	11	9.513
	B	4,7	9.522, 9.525 <sup>b</sup>
	C	1	9.520
	D	12	9.529
4	A	8	9.519
	B	6	9.498
	C	10	9.512
	D	3	9.524
Average			9.518 ± 0.007
s			0.011
s of mean			0.003

<sup>a</sup>Samples were run in sets of six

<sup>b</sup>Duplicate samples run on different days

Bromine was determined both by the micro-Carius method and by the macro-sodium peroxide bomb fusion method. At least one determination was made by each method on each of the six test samples.

Using the Carius method, accurately weighed 10 mg samples were digested in 0.5 ml of fuming nitric acid and 15 mg of silver nitrate for 12 h at 250 °C. After cooling, the tubes were opened and the contents diluted with water. Following a digestion period, the silver bromide was filtered on a weighed micro-filter tube.

Using the sodium peroxide bomb method, 275 mg samples were mixed with 15 g of sodium peroxide-sugar mixture (14:1) in a Parr peroxide bomb and ignited. The resulting melt was washed from the bomb and the solution boiled to destroy peroxides. Hydrazine sulfate was added to reduce any bromate present. The solution was made acid with nitric acid and sufficient 0.1 N silver nitrate solution was added to precipitate all of the bromide. The precipitate was filtered off and redissolved in concentrated ammonium hydroxide solution and reprecipitated by the addition of silver nitrate and nitric acid.. This precipitate of silver bromide was collected on a weighed fritted-glass filter. Blanks were run with each set. In addition, two samples of Chlorobenzoic Acid SRM 144 were taken through the same procedure. Values of 22.63 and 22.61 percent chlorine were obtained to be compared with the theoretical value of 22.65 percent chlorine.

The analytical results are given in Table 14. There is no significant difference between the bromine content found by the two methods. The average value, based on all determinations is  $39.80 \pm 0.05$  percent, where the uncertainty is given at the 95 percent confidence level. The theoretical value for bromine is 39.75 percent.

Table 14. Bromine content of o-bromobenzoic acid, SRM 2142.

Carius method		Bomb method	
Bottle No.	Percent bromine	Bottle No.	Percent bromine
7	39.80	11	39.89
10	39.85	7	39.70
2	39.98	2	39.81
7	39.68	4	39.92
10	39.88	7	39.74
11	39.91	2	39.74
12	39.72	4	39.78
4	39.78		
2	39.67		
mean	39.81	mean	39.80
s	0.11	s	.08
s of mean	.04	s of mean	.03

#### E. Fluorine Content of Orchard Leaves SRM 1571

Fluorine has been determined in Orchard Leaves SRM 1571. The method used was the "Tentative Method of Analysis for Fluorine Content of the Atmosphere and Plant Tissues (Manual Methods) 12204-01-68T" adopted by the Intersociety Committee [19]. This is the method that will probably find wide usage in air pollution analyses of fluoride damage of plants and for which the present SRM may be useful as a standard. Briefly the method is as follows: A dry sample of leaves (10 to 15 g) is weighed in a platinum dish and then made alkaline with a calcium oxide slurry. The treated leaves are heated on a hot plate until charring and partial ashing takes place. The ashing is completed in a muffle furnace at 600 °C. The entire residue or a weighed portion of it is fused with sodium hydroxide to convert all the fluoride to a soluble form. The melt is disintegrated in hot water and transferred to a Huckabay still [20]. The tentative method given above calls for a Willard-Winter distillation.

The Huckabay still has a jacket containing boiling tetrachlorethane to maintain a distillation temperature of 145 °C. Sulfuric acid was used instead of perchloric acid in the still. 250 ml of distillate was collected for the spectrophotometric analysis. An additional 35 ml was usually collected to be certain that all the fluorine had distilled. The fluoride was determined in an aliquot (usually 35 ml) of the distillate using the lanthanum-alizarin complexone spectrophotometric method.

When 10-g samples were weighed, the entire residue was used for distillation. With 50-g samples, a weighed portion (approximately 1/5) of the melt residue was distilled. In this case, more than one distillation could be made from the same sample. Usually two were made. In addition, more than one spectrophotometric determination was made on each distillate.

Fluorine blanks were run on the reagents used and amounted to about 4 µg for a 10-g sample or its residue equivalent. Each time a spectrophotometric determination was made, a standard

series was also run. This standard series contained from 0 to 50  $\mu\text{g}$  in 50 ml. It was prepared from a stock sodium fluoride solution. The curve would vary from day to day and also with new batches of lanthanum-alizarin complexone reagent.

A number of runs were made to determine the efficiency of the distillation process. Three solutions, each containing 100  $\mu\text{g}$  of F, were distilled under conditions identical to those of the analysis. Spectrophotometric determination of the fluoride gave the results listed below, where the multiple numbers indicate results for aliquots.

<u>Run Number</u>	<u>Fluorine Recovered, <math>\mu\text{g}</math></u>
1	112, 103
2	97, 96
3	108

The results of determination of the fluorine, using six samples of the SRM are given in Table 15. The multiple results given for several of the samples are those found for aliquots of the distillates. The overall average, giving each sample equal weight, is 3.9 ppm.

Six determinations were made in which the melt was acidified with perchloric acid, prior to distillation. The results gave an average value of 5.5 ppm which is slightly higher than the average found using sulfuric acid.

Several laboratories have analyzed this SRM using a variety of methods and have kindly sent us their results. The methods used and the results reported are given in Table 16. It is a pleasure to recognize the following in this respect.

L. L. Porter, Anaconda Aluminum Company, Columbia Falls,  
Montana

A. J. Ellis, Department of Scientific and Industrial Research,  
New Zealand

Walter Oyung, Bay Area Air Pollution Control District, San  
Francisco, California

D. T. Taves, University of Rochester School of Medicine and  
Dentistry, Rochester, New York



Table 15. Fluorine content of orchard leaves, SRM 1571.

Sample number	Weight of sample	Weight of residue used	Net fluoride $\mu\text{g}$	F ppm	
1	10.42 g	A11	34	3.3	3.5
			38	3.7	
			36	3.5	
2	10.29 g	A11	34	3.3	3.5
			38	3.7	
			36	3.5	
3	40.00 g	Total residue = 4.502 g			4.2
	<u>a</u>	1.157 g	167	4.1	
			177	4.4	
4		<u>b</u>	1.187	154	3.8
	41.16	Total residue = 4.28 g			4.0
	<u>a</u>	1.077	163	4.0	
5	43.37	Total residue = 5.56 g			4.4
	<u>a</u>	1.237	175	4.0	
			209	4.8	
		<u>b</u>	1.320	193	4.4
			193	4.4	4.4

Table 16. Fluoride content of SRM 1571 report by several laboratories.

Laboratory	Method	Fluoride, ppm
A	Technicon AutoAnalyzer (HClO <sub>4</sub> )	8
	Technicon AutoAnalyzer (H <sub>2</sub> SO <sub>4</sub> )	3
B	Micro-diffusion	2.5
	Pyrohydrolysis	4.4
C	Oxygen flask - fluoride electrode	5.6
D	Micro-diffusion	5.9

(W. P. Schmidt, R. A. Paulson)

## 9. FIRE RESEARCH PROGRAM

A study to determine the nature and extent of toxic gases present in fire-fighting situations was undertaken under the sponsorship of the Office of Fire Research and Safety at NBS. This study is part of a larger program being conducted by the sponsor to develop better breathing support systems for firemen. An extensive survey was made of pertinent literature and the information obtained was summarized and interpreted. This will be published as a National Bureau of Standards Report "Toxic Atmospheres Associated with Real Fire Situations". It is concluded that fires can produce extremely hazardous atmospheres and that good respiratory protection is essential for anyone involved in a fire situation. An outline of the report, essentially the table of contents, is given in Table 17. A brief summary of each section is given in the following discussion.

Table 17. Toxic atmospheres associated with real fire situations.

- I. Introduction
- II. Statistics on Casualties
- III. Review of Some Experimental Results
- IV. Specific Toxic Materials Produced in Fires
  - A. Carbon Monoxide
  - B. Oxygen Deficiency
  - C. Carbon Dioxide
  - D. Hydrogen Chloride
  - E. Hydrogen Cyanide
  - F. Nitrogen Dioxide
  - G. Phosgene
  - H. Sulfur Dioxide
  - I. Ammonia
  - J. Hydrogen Sulfide
  - K. Miscellaneous Halides and Halogens
  - L. Other Irritants
  - M. Miscellaneous Simple Asphyxiants and Gases with Anesthetic Effects
  - N. Smoke
  - O. Combinations of Toxic Gases
- V. Recommendations and Conclusion
- VI. References

The Introduction emphasizes that the atmosphere we breathe must be within certain limits for normal psychological and physiological processes to be maintained. While there is a great lack of knowledge concerning combustion and the atmosphere created by fires, there is no doubt that dangerous combustion products result.

Section II, concerning statistics on fire casualties, gives the results of several U. S. and British surveys. The British surveys appear to be thorough, however several of the U. S. surveys, in order to provide more useful information, should be better founded statistically. Most surveys show toxic gases or smoke to be a significant cause of fire casualties.

Section III reviews some experimental results on measurement of toxic gases prevalent in fire situations. Various types of fire tests have been performed in which fire gases have been analyzed. These range from burning materials in small flasks to the burning of full sized structures. Most fire tests on common materials and structures indicate that such atmospheres are deficient in oxygen and contain CO and excess CO<sub>2</sub>. Increasing ventilation usually favors production of CO<sub>2</sub> rather than CO.

In a few studies on burning materials, gases such as HCN, HCl, HF, SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and Cl<sub>2</sub> have been determined. Except for HCl, which may be formed in relatively large quantities from polyvinyl chloride, the above mentioned gases are usually not found in fire atmospheres in concentrations as high as CO or CO<sub>2</sub>. Several full scale fire tests are described in which CO, CO<sub>2</sub> and O<sub>2</sub> were monitored in certain locations as a function of time. These show that oxygen can be depleted to the 3-4 percent level, CO<sub>2</sub> can reach 14 percent or higher, and CO can reach 4 percent or higher.

Specific toxic gases produced in fires are discussed in Section IV, where feasible, from the standpoint of physiological

and psychological effects, formation in fires, and characterization of a situation in which the gas might be produced. In fire atmospheres, high concentrations of  $\text{CO}_2$  and CO are usually found simultaneously with low  $\text{O}_2$  concentrations.

Carbon monoxide is produced from the incomplete oxidation of carbonaceous materials in virtually all fire situations. Carbon monoxide, when respired by humans acts as a chemical asphyxiant, that is, it prevents the hemoglobin of the blood from absorbing oxygen. One percent CO in respired air would be lethal for exposure of less than one minute. Experimental data indicate CO could easily be present at the 3-4 percent level in a real fire. Poor ventilation in a fire situation favors CO formation.

Combustion of materials decreases the oxygen concentration in the immediate surroundings. Deficient oxygen in a respired atmosphere causes symptoms such as loss of muscular coordination and psychological disturbances. An oxygen concentration of about 6 percent or lower is rapidly fatal. This level can be reached in fires as various studies have shown.

Carbon dioxide is formed in combustion of carbonaceous materials. Respiration of 10-12 percent  $\text{CO}_2$  in air for more than a few minutes is fatal due to paralysis of the respiratory center of the brain. Carbon dioxide may be present at the above level in fires.

Hydrogen chloride must be considered in a fire situation because plastics containing chlorine, when heated to sufficient temperature in a fire, evolve hydrogen chloride. The large and increasing use of polyvinyl chloride plastics makes HCl a more common constituent of fire gases today than in the past. Hydrogen chloride is a respiratory irritant which is easily detected by its odor before lethal concentrations are reached.

Hydrogen cyanide is formed, usually in small amounts, in fires involving nitrogen containing materials such as wool, nylon, and urethanes. It acts as a chemical asphyxiant when respired and is rapidly fatal at concentrations of about 3000 ppm.



Nitrogen dioxide and phosgene are respiratory irritants and on inhalation of sufficient quantities may cause injury or death due to pulmonary edema. Nitrogen dioxide is formed when nitrogen containing materials such as polyamides and wool are burned. Phosgene may be evolved from burning chlorine-containing plastics. Sulfur dioxide, ammonia, hydrogen sulfide, halides, halogens and other irritants may be formed, generally in rather small amounts, on combustion of appropriate materials. These gases are classified as irritants and usually are easily perceived by their irritating effects or odors.

Simple asphyxiants and gases with anesthetic effects are discussed but are not of great importance in the usual fire atmosphere.

Smoke, namely particulate matter and any absorbed materials, when inhaled usually causes a mild irritation of the respiratory tract. Smoke particles when swallowed after lodging in the pharynx may cause nausea and vomiting. Smoke is evolved from nearly all materials during the combustion process, especially under conditions of poor ventilation.

Combinations of high concentrations of toxic gases and an oxygen deficient atmosphere usually occur simultaneously in most fire situations. This is well illustrated by several figures and tables shown in the report. The physiological and psychological effects of a combination of toxic gases may be additive, synergistic, or antagonistic. If additive, the overall effect of the combination represents the sum of the individual effects, if synergistic, the overall effect is much greater than the sum, and if antagonistic, the overall effect is less than the sum. Several studies on animals show that different combinations of CO, CO<sub>2</sub>, and O<sub>2</sub>, varying from normal, generally produce additive effects. The addition of small amounts (less than 100 ppm) of HCl, NO<sub>2</sub>, SO<sub>2</sub>, or HCN to atmospheres containing various combinations of CO, CO<sub>2</sub>, and O<sub>2</sub> is found to cause effects which are synergistic.

Section V concludes the report and makes recommendations on how the problem of toxic gases in fires might be better elucidated. More valid statistical methods and standardized report forms would help to more clearly define many aspects of the toxic gas problem as it exists in the U. S.

It is concluded that a combination of toxic gases and oxygen deficiency, and not CO alone, is the real hazard of a fire atmosphere. The respiratory function, then, must be protected against not only CO, but many other gases as well.

There are many variables involved in each individual fire situation, and this makes difficult the accurate prediction of the content of a fire atmosphere. Since new materials and changes in quantities of traditional materials are used in furnishings and construction of buildings, the usual fire atmosphere of today may vary considerably from that in the past or future. Measurement of toxic gas concentrations at actual fires using indicator tubes or other measurement devices would help to better characterize fire atmospheres.

The concentrations at which a toxic gas or combination of toxic gases exerts deleterious psychological or physiological effects depends greatly upon such individual characteristics as age and health. More work is necessary to determine the effects of various combinations of toxic gases and the mechanism of any synergistic action which may be involved.

Firemen should know what toxic gases to expect in a fire situation and what effects these gases might exert. They should learn to assess a fire atmosphere from visual observation of the surroundings and from odors or irritating effects produced by gases present in the atmosphere.

(J. M. Ives, E. E. Hughes, J. K. Taylor)

## 10. INTERNATIONAL GRANTS PROGRAM

Two programs, funded under the International Research Grants Program, are being carried out as an extension of the research interests of the Section, and for which the Section Chief is NBS monitor. One at the Technion has been in existence for six years. A new one at the University of Zagreb has just been approved.

### A. Program at the Israel Institute of Technology

The National Bureau of Standards awarded a grant to the Technion Research and Development Foundation - Israel Institute of Technology in 1965 to investigate electroanalytical techniques for trace analysis. This work, now in its sixth year, is under the supervision of Professor Magda Ariel. The initial studies, dealing with development of improved electroanalytical techniques, have been summarized in earlier Progress Reports [16,18]. The recent investigations, including those currently in progress, are reviewed in the following sections.

#### 1. Trace Analysis by Anodic Stripping Voltammetry

In the course of this work, undertaken to further the exploitation of the analytical potential of anodic stripping voltammetry (ASV), two new tools have been developed:

- a. The Rotated, Nickel Based, Mercury Film Electrode (MFE) and
- b. The Flow Cell

The MFE has been investigated and its behavior compared to the prevalent Hanging Mercury Drop Electrode (HMDE) from both theoretical and practical points of view, including discussion of those points where the MFE diverges in practice from theoretical behavior. Among the numerous experimental parameters examined, the most important were: (a) the deposition of the mercury film, its thickness, uniformity, stability, criteria of malfunction, *etc.* Stated succinctly:



the MFE shows improved sensitivity, better resolution of adjacent current peaks and, due to its ruggedness, is preferable whenever the analytical procedure requires vigorous solution stirring or electrode transfer (Medium Exchange without Flow Cell): on the other hand, it has relatively higher residual current than the HMDE, a narrower useful potential range and a limited lifetime, often shortened further by the presence of seemingly innocuous solutes. Best results are obtained with the mercury film deposited on a nickel substrate; complete details of construction, coating, operation and applications to the analysis of complex samples were reported.

Intermetallic compounds formed in the mercury (amalgam) phase, either between the mercury and other metals or between the metals dissolved in it, have been discussed. This phenomenon, first encountered in stripping voltammetry with mercury drop electrodes suspended from metal (Pt, Au, *etc.*) wires, and usually regarded as an interference, may be exploited for trace analysis; the depression of the zinc stripping current by platinum has been shown to provide a sensitive means for the estimation of traces of  $\text{Pt}^{+4}$  in solution ( $10^{-7}\text{M}$  and less - *e.g.* the zinc stripping current obtained, under certain, defined conditions with a 8 ppb  $\text{Zn}^{+2}$  solution, is decreased by 10 percent by the presence of 4 ppb  $\text{Pt}^{+4}$ ). A linear correlation between this depression effect and  $\text{Pt}^{+4}$  concentration provides the basis for the latter's quantitative estimation.

The choice of supporting electrolyte from which pre-electrolysis is carried out is often dictated by the composition of the sample and is unsuited to the subsequent stripping step for one or more of the following reasons: unsatisfactory resolution, interferences present in relatively high concentrations, highly sloped base current, *etc.* The situation may be improved by effecting a Medium Exchange, *i.e.* transferring the electrode into a more suitable electrolyte before the stripping



step. The Flow Cell developed in the present work permits this transfer to be effected without either breaking the electrical circuit or exposing the electrode to the atmosphere, thus, preventing losses hitherto connected with this step; metals such as zinc, which could not be determined by Medium Exchange are now easily determinable.

The usefulness of the Flow Cell has been demonstrated through a series of determinations of trace amounts of lead and copper carried out in a number of standard steel samples. These analyses are characterized by the ease and speed of the procedure involved: due to the Flow Cell, analysis is carried out directly on the sample solution, without recourse to preliminary separation steps. Contamination risks are reduced considerably.

The Flow Cell has also been combined with an ion-exchange chromatographic column to provide an anodic stripping analogue of "chromatopolarography". This combination constitutes a convenient and sensitive means for obtaining elution parameters.

The Flow Cell may also serve as the monitoring part of a continuous analytical system, with the appropriate electrode choice, according to the analyte involved; due to its construction, the cell lends itself to convenient intermittent standardization, by simply diverting the flow from the analyte to the standardizing solution.

The complex samples analyzed by anodic stripping voltammetry included: (a) zinc in silicates and rocks; (b) trace metals (Zn, Pb, In, Cd, Cu) in standard glasses; (c) copper and lead in standard steels. The procedure developed for zinc in silicates, described and discussed in detail, served to illustrate the careful and considered technique required for successful trace analysis.

The controlled purity of the reagents and especially of the water employed was essential to the success of the project;

an effective purification system for distilled water was described in detail [18].

Sensitive and selective trace determinations in complex samples can be effected by stripping voltammetry combined with the judicious use of these tools.

Six publications have resulted from the above described activities [21-26].

## 2. Spectrophotometric Studies at Optically Transparent Electrodes

This new project, directed at evaluating the potentialities of combined voltammetry and attenuated total reflectance spectrometry (ATR) at optically transparent electrodes as a source of data concerning organic electrode reactions, has gotten off to a good start. Results to date include:

- a. Design of a suitable electro-optical cell.
- b. Methodology for preparing the semi-transparent electrodes.
- c. Investigation of potential distribution on the electrode as related to cell geometry
- d. Investigation of absorbance changes in metal film due to potential modulation
- e. Investigation of parameters affecting film "life-time" and stability.

The internal reflection technique applied in this work permits spectrophotometric observation of a region extremely close to the surface of a transparent electrode during an electrochemical process.

The electrochemical-optical cell was designed according to the one proposed by W. N. Hansen [27] with some modifications that help in fixing its exact position in the spectrophotometer sample holder in a very reproducible way.

The main part of the cell used is the transparent electrode. Three types of electrodes were used: Gold film electrodes produced by vacuum evaporation technique (with  $\text{Bi}_2\text{O}_3$  as inter-

mediate layer), platinum film electrodes evaporated directly on glass from a W wire, and a gold film commercial electrode.

Two types of phenomena specific for the thin film electrodes were investigated in order to understand the special behavior of this experimental system: (I)  $iR$  drop in the film; (II) absorbance changes in the absence of any absorbing - species and/or any faradaic process.

The "reversible" system  $[Fe(II) - Fe(III) \text{ dimethylortho-phenanthroline complexes}]$  was used as a model for measuring the extent of potential inhomogeneity on the electrode surface.

It could be shown experimentally, by measuring the potential changes at maximum distance on the film from the controlled point, that for millimolar solutions the current densities resulting at 20-50 mV/sec scans do not cause severe distortion of equipotential conditions. For 10 mM solutions it was proved advisable to use only narrow strips of the film to avoid considerable  $iR$  drops even at low rates of potential scanning.

The deterioration rate of the film proved to be very sensitive to high current densities. It was shown that the deterioration is gradual and is severest near the electrical connections to the film. This gradual corrosion of the film causes a gradual increase in the extent of the  $iR$  drop in the film during its "life-time". In the subsequent development of any analytical method, this will have to be taken into account and checked by frequent "standard" runs with well defined systems.

Absorbance changes of the internal reflected beam due to modulated potential of the film electrode were monitored at both types of the gold electrodes used. In both cases the amplitudes and signs of the changes could be related to the spectrum of the metallic film (which was different for each type). It could be proved that the effect of the applied potential is the modulation of the energy level of the free



electrons in the film, causing a shift in the optical parameters of the film, and resulting in a shift of several nm in the spectrum obtained. (These results were in accordance with the theory proposed for the a.m. phenomenon [28].

The following manuscripts have been submitted for publication:

"Processes in Solution and on the Electrode Surface Monitored by IRS with Metal Film Electrodes", Part I, General Considerations, Part II, The Oxidation of dimethylferrin--the case of a simple faradaic reaction, Gottesfeld, S. and Ariel, M., submitted to the *J. Electroanal. Chem.*

"Processes in Solution and on the Electrode Surface Monitored by IRS with Metal Film Electrodes", Part III, The Oxidation of Tetramethylbenzidine--an electrochemical reaction with stepwise electron removal, Gottesfeld, S. and Ariel, M., submitted to the *J. Electroanal. Chem.*

"Processes in Solution and on the Electrode Surface Monitored by IRS with Metal Film Electrodes", Part IV, The Oxidation of Malachite Green--a case where reflection adsorbance is dominated by the contribution of the adsorbed layer, Gottesfeld, S. and Ariel, M., submitted to the *J. Electroanal. Chem.*

"Electro-Optical Study of the Oxidative Adsorption of 1-Naphthol on Platinum or Gold Electrodes", Laser, D. and Ariel, M., submitted to the *J. Electroanal. Chem.*

The electrochemistry of bilirubin in dimethylsulfoxide is being studied by a variety of methods (polarography, controlled potential coulometry, potential scanning at a rotating platinum electrode). This preliminary work is intended as preparation for a thorough electro-optical study of bilirubin.

### 3. Anodic Stripping Voltammetry in Propylene Carbonate

Propylene carbonate (PDC) dissolves a wide spectrum of organic substances; its usefulness in polarography has been mentioned (*e.g.*, Gutman *et al.* in *Monatsh. Chem.* 99, 699 (1968)). ASV in such a medium, if feasible, should allow in certain cases the direct determination of metal traces in organics (without



preliminary ashing). With this objective in mind, problems involving the methodology of working in this medium have been investigated, and the following conclusions arrived at:

a. The risk of sample contamination through the reference electrode may be minimized by employing a silver wire dipped into a saturated solution of tetraethyl-ammoniumiodide in PDC, with a "thirsty glass" junction.

b. Vacuum distilled PDC retains approximately  $10^{-4}$ M water; this, while negligible for polarographic purposes, where relatively high ( $10^{-4}$ M or higher — see Gutmann *et al.*, *loc. cit.*) metal ion concentrations are involved, prevents its use for the ASV determination of alkali and alkaline earth metals (as a result of the high residual current, ASV in PDC is restricted to a rather narrow potential range).

c. Available, suitable supporting electrolytes are not sufficiently pure to satisfy ASV criteria; however, the linear correlation between  $i_p$  (peak current in ASV) and metal ion concentration has been shown to hold for  $10^{-5}$ M —  $10^{-7}$ M  $Zn^{+2}$  or  $Cd^{+2}$  solutions (both in water and in PDC) deposited and redissolved in the absence of added supporting electrolyte. Due to the considerable ohmic drops involved (of the order of several hundred mV), the shape of the stripping peaks is, naturally, severely distorted; their width causes considerable overlapping, so that the method will probably be inapplicable to the analysis of mixtures.

(M. Ariel)

#### B. Program at University of Zagreb

A project "Electrochemical Study of Metal Ion-Ligand Interactions in Nonaqueous Solutions by Investigation of Electrochemical Properties of the Ligand" to be conducted at the University of Zagreb, Yugoslavia, was approved under the International Research Grants Program. Professor Ivan Piljac of the Institute of Inorganic Chemistry, Faculty of

Technology, University of Zagreb, is the principal investigator and John K. Taylor is the Project Monitor for NBS. The project will begin about September 1, 1971.

The investigation seeks to find correlations between the strength of metal ion-ligand interactions and changes of electrochemical properties of the ligands. Studies will be made on hydroxyquinones and their conjugate bases in nonaqueous media by polarography and other electrochemical methods. Electrochemical measurements will be combined with spectroscopic ones, using a thin layer optically transparent electrochemical cell.

(John K. Taylor)

## 11. PERSONNEL AND ACTIVITIES

### A. Personnel Listing

John K. Taylor, Section Chief

Alberta L. Nichols, Secretary

#### Staff

Ernest E. Hughes

Julian M. Ives

Richard H. Johns (Research Associate)

William D. Kinard

Rolf A. Paulson

William P. Schmidt

### B. Publications

1. J. K. Taylor, Editor, "Microchemical Analysis Section Summary of Activities", NBS Technical Note 545, October 1970.

2. C. E. Champion, G. Marinenko, J. K. Taylor, and W. E. Schmidt, "Determination of Sub Microgram Quantities of Chromium by Coulometric Titrimetry", *Anal. Chem.* 42, 1210 (1970).

3. J. K. Taylor, "Electrochemical Methods of Microchemical Analysis", Proceedings, VI International Symposium on Microchemistry, Vol. D, p. 173, Verlag, Wiener Medizinischen Akademie (1970).

4. E. E. Hughes and W. P. Schmidt, "Sulfur Dioxide Permeation Tube, SRM 1625", Certificate of Analysis, NBS Office of Standard Reference Materials, December 1, 1970.

5. R. A. Paulson and W. P. Schmidt, "Urea, SRM 2141", Certificate of Analysis, NBS Office of Standard Reference Materials, August 28, 1970.

6. R. A. Paulson and W. P. Schmidt, "O-Bromobenzoic Acid, SRM 2142", Certificate of Analysis, NBS Office of Standard Reference Materials, September 1, 1970.

7. W. P. Schmidt and R. A. Paulson, "Sulfur in Residual Fuel Oil, SRM 1623", Certificate of Analysis, NBS Office of Standard Reference Materials, April 7, 1971.

8. W. P. Schmidt and R. A. Paulson, "Sulfur in Distillate Fuel Oil, SRM 1624", Certificate of Analysis, NBS Office of Standard Reference Materials, April 7, 1971.

C. Talks

1. J. K. Taylor, "Electrochemical Methods of Microchemical Analysis". VI International Symposium on Microchemistry, Graz, Austria, September 1970.

2. J. K. Taylor, "Trace Analysis by Electrochemical Methods", American Chemical Society National Meeting, Los Angeles, California, April 1971.

3. E. E. Hughes, "Fundamentals of Gas Analysis", Instrument Society of America, 17th National Aerospace Symposium, Las Vegas, Nevada, May 1971.

D. Committee Activities

J. K. Taylor

Service Analysis Coordinator, Analytical Chemistry Division Member, Review Board, Science Book List, American Association for the Advancement of Science Elected member, Council of the American Chemical Society (ACS)

Member, Panel on Chemistry, Civil Service Board of Examiners

Member, Board of Managers, Chemical Society of Washington

Member, Advisory Committee, Laboratory Guide, American Chemical Society

Chairman, Chemical Education Topical Group, Chemical Society of Washington

Member, ISO/TC 48 Laboratory Glassware and Related Apparatus



Member, Advisory Panel, NBS Measurements for Air  
Quality Program

Member, Advisory Panel, Chemical Technology Journal

Member, Visiting Committee, GSA National Laboratory

Associate Member, IUPAC Commission V.5, Electro-  
analytical Chemistry.

R. A. Paulson

Member, Service Analysis Committee, Analytical  
Chemistry Division, NBS

Collaborator, Committee for Study of Microchemical  
Methods, Association of Official Agricultural  
Chemists

W. P. Schmidt

Collaborator, Committee for Study of Microchemical  
Methods, Association of Official Agricultural  
Chemists

Collaborator, Carbon, Hydrogen and Nitrogen Methods  
Commission on Microchemical Techniques, IUPAC

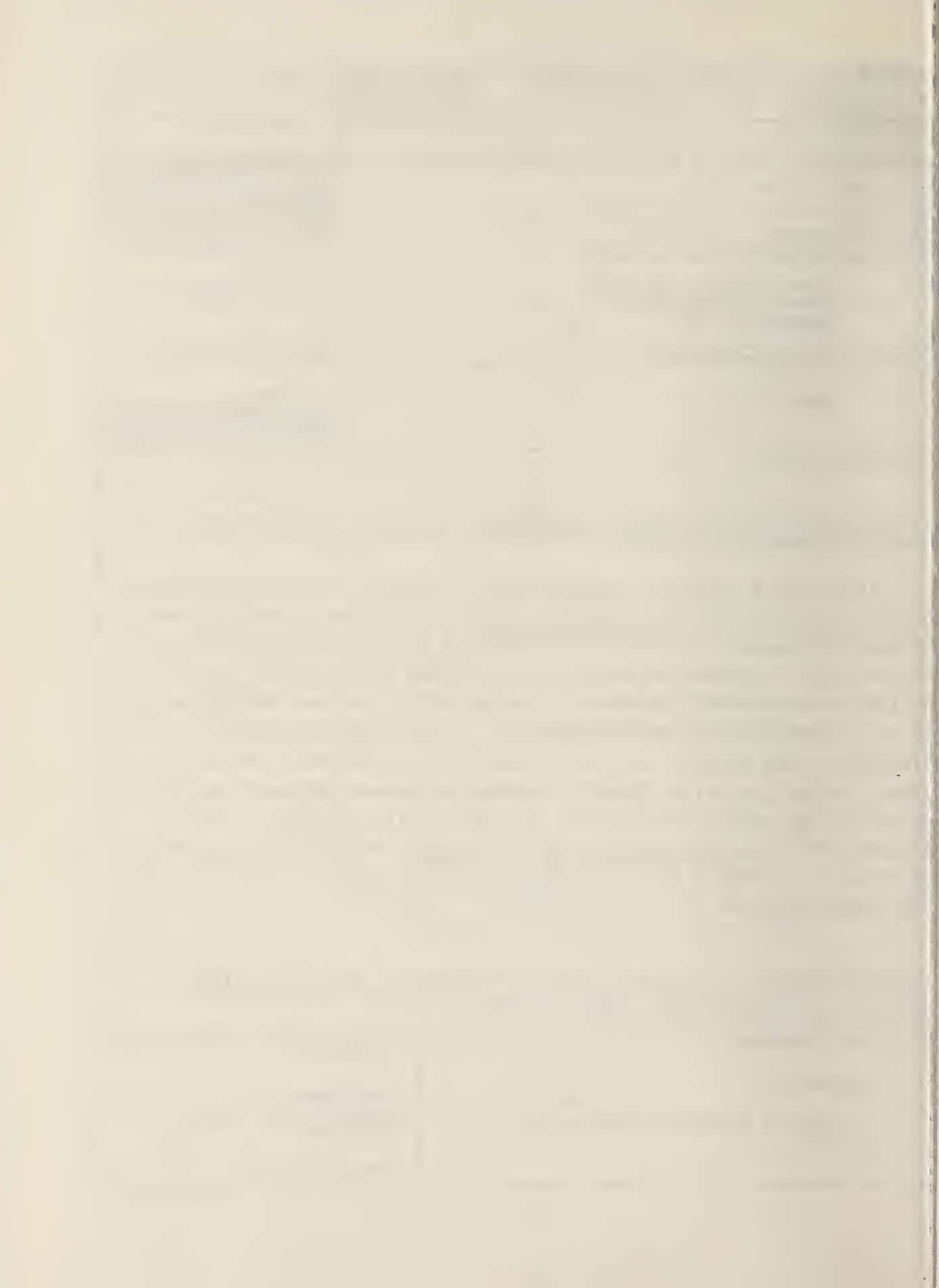
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